ORSAY
Série
N° d ordre

1725

THÈSE

présentée a

l'UNIVERSITE DE PARIS-SUD
CENTRE D'ORSAY

pour obtenir le grade de

docteur es-sciences

par

Christian KUBACH

SUJET DE LA THESE :

ETUDE THEORIQUE DES PROCESSUS ELASTIQUE ET D'ECHANGE DE CHARGE DANS LES COLLISIONS DE PROTONS SUR DES ATOMES DE GAZ RARES.

Soutenue le 20.10.76 devant la commission d'examen

L. SALEM	Président
R. Mc. CARROLL	Examinateurs
M. BARAT	
C. MANUS	
J. DURUP	
V. SIDIS	

ORSAY
Série
N° d ordre

THÈSE

présentée a

l'UNIVERSITE DE PARIS-SUD
CENTRE D'ORSAY

pour obtenir le grade de

docteur es-sciences

par

Christian KUBACH

SUJET DE LA THESE :

ETUDE THEORIQUE DES PROCESSUS ELASTIQUE ET D'ECHANGE DE CHARGE DANS LES COLLISIONS DE PROTONS SUR DES ATOMES DE GAZ RARES.

Soutenue le 20.10.76 devant la commission d'examen

L. SALEM	Président
R. Mc. CARROLL	Examinateurs
M. BARAT	
C. MANUS	
J. DURUP	
V. SIDIS	

UNIV.
LEIDEN
BIBL.

REMERCIEMENTS

Je remercie Madame F. Fayard et Monsieur L. Salem, professeurs, pour leur enseignement de second cycle qui a contribué au choix de mon orientation.

Je suis très reconnaissant à Monsieur le Professeur J. Durup de m'avoir accueilli dans son laboratoire et aidé dans l'élaboration de ce travail.

J'exprime toute ma gratitude à V. Sidis, Chargé de Recherches au C.N.R.S., pour son aide quasi-permanente.

Je tiens particulièrement à remercier Messieurs M. Barat, Directeur de Recherches au C.N.R.S., J.P. Gauyacq, Attaché de Recherches au C.N.R.S., B. Stern, Assistant à l'Université de Paris VI et Mesdames C. Benoit, Chargée de Recherches au C.N.R.S. et C. Pernot, Assistante à l'Université de Paris XI, pour leur collaboration amicale, leur participation à l'élaboration de nombreux résultats et les discussions fructueuses auxquelles ils ont bien voulu participer.

Je remercie très vivement Mesdames E. Simonneau, C. Pierrot, R. Barbot et Mademoiselle M. Desbrosses qui ont bien voulu se charger de la tâche ingrate de la dactylographie du manuscrit.

Les chapitres VI et VIII sont partiellement constitués d'articles regroupant des résultats théoriques et expérimentaux. Ces derniers ont été obtenus au laboratoire des Collisions Atomiques par C. Benoit, J. Pommier et M. Barat que je tiens particulièrement à remercier pour cette étroite collaboration.

TABLE DES MATIERES

		Page
I	INTRODUCTION	1
II	RAPPEL SUR LE TRAITEMENT MOLECULAIRE DES COLLISIONS ATOMIQUES. METHODES DE RESOLUTION DES EQUATIONS COUPLEES.	10
	1- Traitement moléculaire des collisions atomiques	10
	1.1. Hamiltonien du système	10
	1.2. Equationscouplées pour le mouvement des noyaux	12
	1.3. Etats adiabatiques ; diabatiques	15
	1.4. Notions pratiques	18
	2- Méthode de résolution des équations couplées	22
	2.1. Séparation des parties radiales et angulaires pour le mouvement des noyaux	22
	2.2. Résolution des équations radiales couplées	22
	2.3. Matrice de diffusion	25
III	ETUDE DU SYSTEME COLLISIONNEL $H^+ - H$	28
	Importance du couplage rotationnel	28
	Sections efficaces différentielles d'excitation de H dans l'état 2 p,dans la collision $H^+ - H$	29
	Discussion et commentaires	34
IV	ETUDE MOLECULAIRE DU SYSTEME COLLISIONNEL $H^+ - Xe$	37
	Introduction	37
	Courbes d'énergie potentielle du système $(H - Xe)^+$	39
	Discussion et commentaires	44

V ETUDE THEORIQUE DE LA DIFFUSION ELASTIQUE DE H^+ PAR Xe 48

1- Introduction 48

2- Diffusion par le potentiel de $X^1\Sigma^+$ 49

3- L'approximation à trois états 50

4- Effet des états moléculaires excités 56

VI PROCESSUS D'ECHANGE DE CHARGE DANS LES COLLISIONS ENTRE PROTONS ET ATOMES DE GAZ RARES. I H^+ + Xe 58

1- Introduction 58

2- Résultats expérimentaux 59

3- L'approche moléculaire 63

4- Résultats théoriques 65

5- Discussion 71

Discussion et commentaires 76

VII ETUDE MOLECULAIRE DU SYSTEME COLLISIONNEL H^+ - Kr 80

1- Introduction 80

2- L'approche LCAO - MO - SCF 81

3- L'approche PVB 84

4- Etats diabatiques pour le couplage spin-orbite 87

Discussion et commentaires 90

VIII PROCESSUS D'ECHANGE DE CHARGE DANS LES COLLISIONS ENTRE PROTONS ET ATOMES DE GAZ RARES. II H^+ + Kr ET SYSTEMES PLUS LEGERS 93

1- Introduction 94

2- Résultats expérimentaux 95

3- Résultats théoriques 98

4- Sections efficaces totales des processus d'échange de charge quasi-résonnant dans les collisions : H^+ + Ar , Ne , He 103

5- Conclusions 108

Discussion et commentaires 135

IX ETATS DIABATIQUES DU SYSTEME COLLISIONNEL H^+ - Xe 141

X CONCLUSION 150

REFERENCES 153

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41548102_0027

Chapitre I

INTRODUCTION

Depuis 1950 environ, de nombreux résultats expérimentaux relatifs aux systèmes collisionnels proton - gaz rares, ont été accumulés. Les premiers travaux /1-5/ portaient sur la mesure des sections efficaces totales d'échange de charge. Ces expériences consistent à déterminer, en fonction de l'énergie de la collision, le nombre total d'atomes H diffusés dans tous les angles, sans discrimination des états électroniques de la collision. De telles données ne permettent d'accéder, à priori, qu'à peu d'informations sur la nature des intéractions entre les partenaires de la collision et sur les mécanismes responsables des processus collisionnels. La spectroscopie de collision /6/, qui consiste à mesurer des sections efficaces différentielles en angle et en énergie, apporte de telles informations. C'est ainsi que dès 1967 Fleischan et Young /7/ mesurent des sections efficaces différentielles angulaires d'échange de charge, pour les collisions H^+ + Kr (sans détermination des états électroniques finals de la collision). L'analyse de ces données de mesure conduit ces auteurs à interpréter les structures observées en termes d'oscillations de type arc-en-ciel ("rainbow") /8/, caractéristiques d'un potentiel attractif et d'interférences dues à l'évolution du système collisionnel sur les voies d'entrée et d'échange de charge. Ils postulent alors l'existence d'un "croisement" de courbes de potentiel qui serait responsable de l'échange de charge.

La mesure des sections efficaces différentielles angulaires élastiques à faible énergie (quelques eV) dans les collisions proton-gaz rare /8-9/ et l'interprétation des structures observées en terme d'oscillations de type arc-en-ciel, ont conduit à une détermination assez précise du puits de potentiel de l'état fondamental des systèmes : $(H - He)^+$, $(H - Ne)^+$, $(H - Ar)^+$ et $(H - Kr)^+$.

La mesure à quelques keV des sections efficaces différentielles élastique , d'excitation et d'échange de charge (global) /11/ a permis d'une part de tester la partie répulsive des courbes d'énergie potentielle des systèmes proton-gaz rare $(H\text{-}GR)^+$ et, d'autre part, de postuler que les processus responsables de l'échange de charge s'effectuent dans un domaine restreint de distances internucléaires. Conjointement, l'utilisation du "modèle de promotion des orbitales diabatiques" /12/ a également permis de préciser que l'échange de charge dans les collisions H^+ - Xe se faisait au voisinage d'un point de croisement entre courbes d'énergie potentielle et que les processus d'excitation dans toutes les collisions H^+ + GR passaient par l'intermédiaire de la voie d'échange de charge.

Très récemment enfin, le développement expérimental de la technique dite de "temps de vol" /13/ a permis la détermination des sections efficaces différentielles angulaires d'échange de charge pour des niveaux déterminés de l'ion de gaz rare ou de l'atome H formés par échange de charge /14/.

Cet important ensemble de résultats, et notamment les plus récents, a motivé l'étude théorique des systèmes collisionnels H^+ - GR que nous présentons ici. Le but des calculs entrepris est double : il consiste d'une part à chercher la confirmation de mécanismes collisionnels prédits antérieurement et, éventuellement, à apporter des informations nouvelles ou complémentaires et, d'autre part, à obtenir des données quantitatives dont la comparaison avec les résultats expérimentaux servira à tester la valeur du formalisme utilisé, des approximations et des modèles mis en jeu.

Nous nous intéresserons principalement au processus élastique et à l'échange de charge quasi-résonnant :

$$H^+ + GR\ (np^6) \rightarrow \begin{cases} H^+ + GR\ (np^6) \\ H\ (1s) + GR^+\ (np^5) \end{cases}$$

Ce type de réactions pour lesquelles des résultats expérimentaux sont disponibles, se prête à un ensemble d'études théoriques qui permet de dépasser le cadre des collisions H^+ + GR.

C'est ainsi que l'on sait calculer la section efficace de diffusion élastique par un potentiel, au moyen d'un développement en ondes partielles /15/ (cf chapitre II), quantiquement ou en utilisant la méthode J W K B* /16/. La comparaison entre les sections efficaces différentielles calculées et les résultats expérimentaux constitue un test très sensible pour la valeur des puits de potentiel provenant d'un calcul moléculaire ; ceci lorsque l'approximation à un état est valable, c'est-à-dire généralement à faible énergie de collision. Ainsi, les puits de potentiel des systèmes $(H - He)^+$ /17-18/, $(H - Ne)^+$ /19/, $(H - Ar)^+$ /20/ ont été testés, en général avec succès (cf respectivement les références /8, 21, 20/). Nous complétons ici la série H^+ - GR par une étude similaire des systèmes H^+ - Xe (chapitre V) et H^+ - Kr (chapitre VIII).

L'échange de charge quasi-résonnant a fait, depuis les travaux originaux de Stueckelberg /22/ et de Rosen et Zener /23/ l'objet de nombreuses recherches. Dès 1932, Rosen et Zener obtenaient une expression de la probabilité d'échange de charge, en fonction du paramètre d'impact, faisant apparaître explicitement des quantités importantes telles que l'expression et la durée du couplage responsable de la transition ainsi que l'écart énergétique des niveaux impliqués dans le processus (défaut de résonance).

Gurnee et Magee /24/, traitant le problème de l'échange de charge résonnant dans la collision H^+ - H dans une approche atomique, mettent l'accent sur le comportement exponentiellement décroissant du couplage avec la distance internucléaire R. En vue d'une généralisation à d'autres systèmes, ces auteurs proposent l'utilisation d'orbitales atomiques de type hydrogénoïde (cf chapitre VIII). Cette méthode a été étendue par Rapp et Francis /25/ au calcul des sections totales d'échange de charge dans les collisions H^+ + GR.

Quelques années plus tard, Demkov /26/ réussit à exprimer simplement la probabilité d'échange de charge pour deux états ayant des courbes de potentiel parallèles et étant couplés par une intéraction exponentiellement décroissante. Ce résultat est en fait très voisin de celui obtenu par Rosen et Zener /23/, trente ans plus tôt.

---

*Jeffreys Wentzel Kramers Brillouin

Une des caractéristiques du modèle de Demkov est la localisation des transitions dans un petit domaine de distances internucléaires autour de R_c défini par la relation de Stueckelberg /22/ :

$$H_{12}\ (R_c) \ = \ \frac{1}{2}\Delta E$$

où H_{12} désigne le couplage et ΔE la séparation énergétique entre les deux courbes de potentiel (défaut de résonance).

Le problème de l'échange de charge résonnant a été également abordé dans une approche moléculaire. Les oscillations de la probabilité de transition, en fonction du paramètre d'impact, /27/ reflètent alors l'évolutio du système collisionnel sur les voies gerade (g) et ungerade (u) dégénérées à R ∞ (cf fig. 1.).

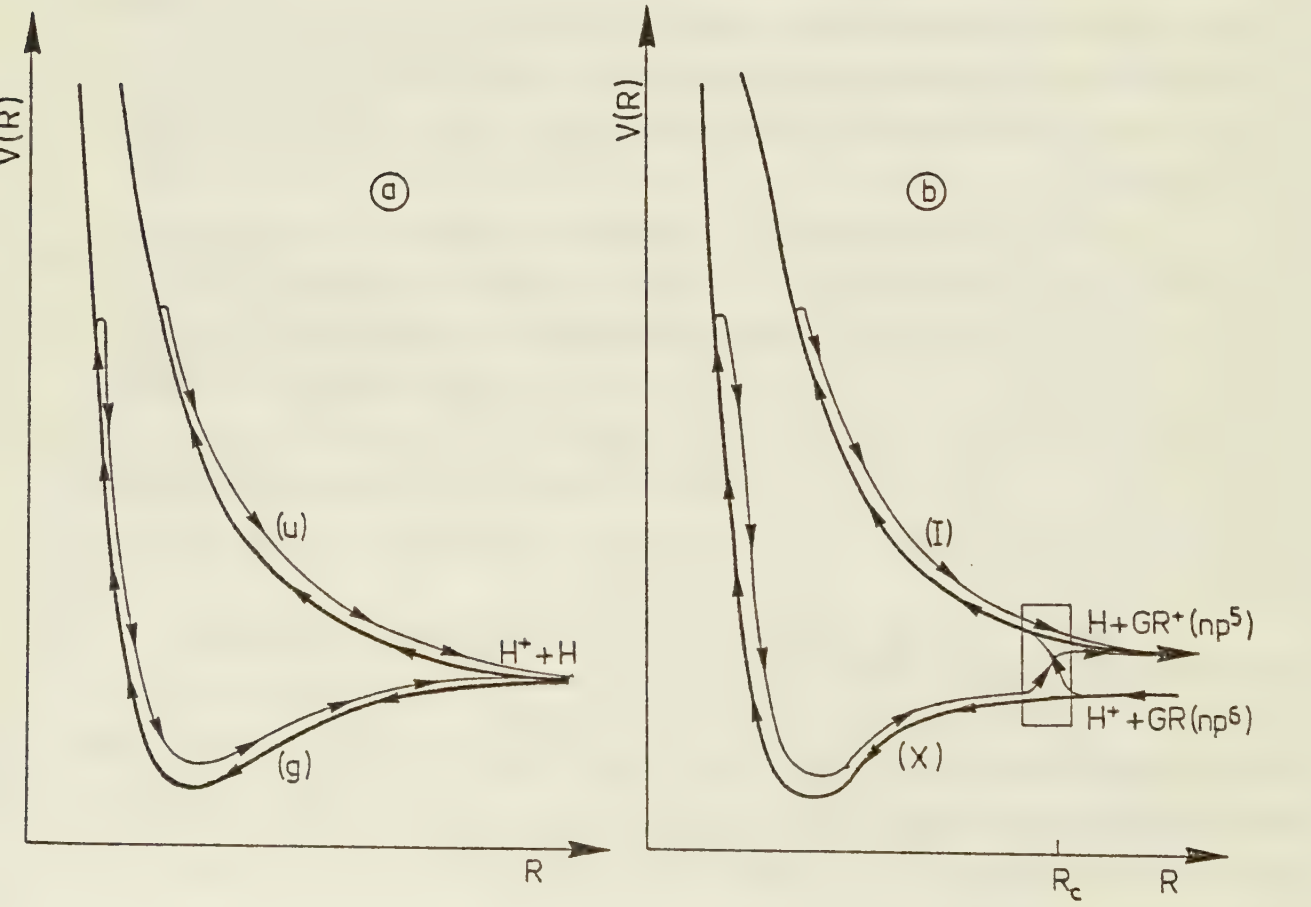


Fig. 1 échange de charge résonnant (a), quasi-résonnant (b).

En fait, cette approche paraît difficilement généralisable à l'étude de l'échange de charge non résonnant où les voies u et g ne peuvent plus être définies. Toutefois, si dans ce dernier cas les transitions s'effectuent à grande distance internucléaire ($R \simeq R_c$ /22/) le système évoluera pour $R<R_c$ sur les voies X et I, avec des probabilités différentes (cf fig. 1) /28/. On voit alors la similitude avec le cas résonnant où le système évolue, avec la même probabilité cette fois, sur les voies u et g. On doit donc, par analogie, s'attendre à observer deux types de structures dans les sections efficaces élastiques et d'échange de charge, du cas non-résonnant :

a) des oscillations de type arc-en-ciel dues à l'évolution du système sur la "voie attractive" (g, dans le cas d'une collision $H^+ - H$, X dans le cas d'une collision $H^+ + GR$).

b) des oscillations dues à l'évolution du système sur les deux voies g et u ou X et I.

De telles structures sont appelées oscillations de type u - g, dans le cas résonnant et oscillations de type Demkov - Stueckelberg, dans le cas quasi-résonnant. Un exemple de ces deux types de structure a été observé dans l'étude du système résonnant $He^+ + He$ /6, 29/ où, à petite énergie de collision, les oscillations de type arc-en-ciel apparaissent à petit angle de diffusion et les oscillations de type u - g à grand angle.

Les idées du modèle de Demkov /26/ ont été appliquées aux systèmes $H^+ + Kr$ et $H^+ + Ar$, par Jonhson et al /30/ qui paramétrisent les courbes d'énergie potentielle (parallèles) sous la forme de potentiels de Coulomb écrantés et qui définissent une intéraction exponentiellement décroissante contenant un paramètre ajustable pouvant être déduit des caractéristiques de la diffusion arc-en-ciel élastique.

Enfin, il convient aussi de citer l'important travail théorique de Shakeshaft et Macek /31/ qui ont montré la possibilité d'obtenir des atomes d'hydrogène à spin polarisés par échange de charge dans les collisions $H^+ + Xe$ et $H^+ + Kr$. Il n'y a, hélas, à l'heure actuelle, aucune expérience venant confirmer ou infirmer leurs prédictions.

Le domaine expérimental et théorique couvert par les problèmes de la collision élastique et d'échange de charge quasi-résonnant dans les

collisions H^+ + GR est donc vaste. Nous présentons ici des calculs ab-initio sur les systèmes H^+ + Xe et H^+ + Kr. Les sections efficaces obtenues seront comparées aux résultats expérimentaux.

En fait, la rapide récapitulation des informations théoriques présentées ci-dessus soulève un certain nombre de problèmes que nous chercherons à résoudre.

Ainsi, s'il existe de nombreux travaux utilisant le modèle de Demkov /26/ (cf par exemple réf. /30,32/), les hypothèses et donc la validité de ce modèle, n'ont pas, à notre connaissance été testées par un calcul ab-initio. Un tel calcul, qui permettra en outre d'apprécier la valeur des intéractions semi-empiriques existant dans la littérature /30, 33/,devra utiliser une approche atomique de la collision.
Cette approche a l'inconvénient de conduire à des états non-orthogonaux à distance internucléaire finie. Par ailleurs, l'utilisation d'orbitales atomiques gelées ne permet pas de décrire la polarisation et la distorsion des nuages électroniques aux petites distances internucléaires.
On conçoit dès maintenant qu'il conviendra d'utiliser deux bases si l'on veut comparer des sections efficaces calculées dans cette approche aux résultats expérimentaux. Une base atomique décrira la collision à grande distance internucléaire. Une base moléculaire, rendant compte du puits de potentiel qui provient du recouvrement des orbitales atomiques et de leur polarisation, décrira la collision à R petit. Au problème de non-orthogonalité des états atomiques, volontairement ignoré par Demkov /26/ vient s'ajouter l'omission par cet auteur du couplage dynamique radial, dû au mouvement des noyaux (cf chapitre II). Cette intéraction peut, en fait, devenir extrêmement importante dans les problèmes de collision. On peut alors se demander s'il y a une façon d'orthogonaliser les états atomiques qui permette de minimiser ce couplage.

Il serait également souhaitable de savoir si la description atomique, utilisant des orbitales atomiques, est mieux adaptée à décrire le phénomène de l'échange de charge quasi-résonnant dans les collisions H^+ + GR, qu'une approche moléculaire utilisant des orbitales moléculaires et éventuellement de connaître les défauts ou les difficultés inhérentes à l'une ou à l'autre de ces deux approches.

Dans la série H^+ + GR, seul le système H^+ + Xe présente un croisement des courbes de potentiel corrélées à H^+ + Xe ($5p^6$) et H + Xe^+ ($5p^5$) /11/. Le cas H^+ - Xe peut-il alors être traité comme les systèmes H^+ + He, Ne, Ar, ou bien constitue-t-il une exception ?

Pour essayer de répondre à ces questions, nous prendrons comme point de départ un traitement moléculaire des collisions atomiques. Une telle description est valable pour des vitesses de collision beaucoup plus petites que celles des électrons de valence, ce qui sera toujours le cas ici. Cette approche contient deux parties :

1) l'obtention d'une base finie et adéquate d'états électroniques

2) la résolution, dans cette base, du système d'équations couplées régissant le mouvement des noyaux.

L'obtention d'une base finie et adéquate est une question pratique qui devra être résolue pour chaque problème collisionnel. En fait, la question de la troncature de la base est souvent inséparable de son caractère "adéquat" (cf. par exemple /35/). On dira qu'une base est adéquate si :

a) elle est de petite dimension

b) les termes de couplage négligés lors de la troncature sont faciles à estimer

c) les termes de couplage dans la base tronquée sont d'une part aisément calculables et, d'autre part, ne deviennent pas trop grands et ne varient trop vite. (Cette dernière condition évite des problèmes d'ordre numérique.)

Si les états adiabatiques (états de la physique moléculaire qui diagonalisent l'hamiltonien électronique) sont aujourd'hui assez faciles à obtenir, avec une assez bonne précision, la difficulté à calculer les éléments de couplage et parfois à tronquer la base /35/, fait que ces états ne seront utilisés ici que pour la description de la collision élastique, à faible énergie, plus précisément dans un traitement à un état de la collision élastique.

Il est reconnu depuis le travail de Lichten /35/ que les états moléculaires adiabatiques ne sont pas les mieux appropriés pour décrire les collisions et on leur oppose souvent des états dits "diabatiques" dont la définition générale demeure un problème (cf chapitre II). Si l'on définit, avec Smith /36/, un sous-espace diabatique, dans lequel les élements de

matrice de l'opérateur impulsion radiale des noyaux sont nuls, on obtient alors un système simple d'équations où les éléments de couplage sont aisément calculables. En fait, il faut voir dans la définition des états diabatiques plus qu'un artifice mathématique (cf chapitre II) puisqu'ils sont bien souvent les états effectivement "suivis" par le système collisionnel /35/.

La résolution d'un système d'équations couplées peut être conduite dans des approches semi-classiques ou quantiques. Dans les méthodes semi-classiques, le mouvement des noyaux est traité classiquement et l'on obtient alors un système d'équations différentielles couplées du premier ordre. En utilisant une trajectoire nucléaire rectiligne, on aboutit à la méthode du paramètre d'impact /37-38/. Les traitements semi-classiques ont été récemment améliorés par l'utilisation d'une méthode dite de "trajectoire commune" /39-40/ où la trajectoire des noyaux est déninie à partir d'un "potentiel moyen" /39-40/. Des résultats utilisant ces deux méthodes sont présentés au chapitre III. Dans le traitement quantique de la diffusion on ne peut plus définir de trajectoire pour les noyaux et l'on obtient un système d'équations couplées du second ordre (cf chapitre II) que l'on résoud numériquement. Le traitement quantique de la diffusion s'est considérablement développé depuis les travaux de Lane et Geltman /41/ et de Gordon /42/.

Nous avons essentiellement utilisé les méthodes quantiques de résolution d'équations couplées. Ces méthodes, notamment celle de Gordon /44/, se sont révélées compétitives (en temps d'ordinateur) avec les méthodes semi-classiques. Dans la comparaison de l'efficacité des méthodes quantiques et semi-classiques, il faut remarquer que les premières ont l'avantage de n'introduire d'erreurs qu'au niveau numérique (erreur de troncature) mais que les secondes permettent une meilleure visualisation du système tout au long du déroulement de la collision.

Le travail présenté ici se construit autour des publications qu'il a occasionnées. La succession d'articles qui seront parfois commentés et discutés montre l'évolution au cours du temps de notre compréhension du problème collisionnel et de notre façon de l'appréhender. Après avoir brièvement rappelé les principes du traitement moléculaire des collisions

atomiques, ainsi que les méthodes de résolution d'équations couplées (chapitre II), nous présentons des résultats sur le système collisionnel H^+ - H qui permet, entre autres, de tester la méthode de résolution des équations couplées (chapitre III). Le chapitre IV est consacré à une approche moléculaire du système collisionnel H^+ - Xe. La base ainsi obtenue est utilisée pour décrire la collision élastique à faible énergie (chapitre V) et l'échange de charge (chapitre VI). Les défauts de l'approche précédente sont évités dans l'étude du système H^+ + Kr où une base d'états diabatiques, ayant une description presque atomique, est construite (chapitre VII). Les sections efficaces obtenues dans cette base sont présentées dans le chapitre VIII qui contient aussi des prédictions sur les systèmes H^+ - Ar, Ne, He. Enfin, le chapitre IX est consacré au traitement diabatique du système H^+ - Xe.

Chapitre II

RAPPELS SUR LE TRAITEMENT MOLECULAIRE DES COLLISIONS ATOMIQUES METHODES DE RESOLUTION DES EQUATIONS COUPLEES

1 - Traitement moléculaire des collisions atomiques :

1.1 - Hamiltonien total du système

Dans un traitement complètement quantique de la collision entre deux atomes A et B, on a à résoudre l'équation de Schrödinger associée à l'hamiltonien (exprimé en unités atomiques dans un système de coordonnées arbitraires, fixé dans l'espace) :

$$H = \frac{1}{2m_A} P_A^2 + \frac{1}{2m_B} P_B^2 + \frac{1}{2} \sum_i P_i^2 - \sum_i \left[\frac{Z_A}{R_{iA}} + \frac{Z_B}{R_{iB}} \right] + \frac{Z_A Z_B}{R_{AB}} + \sum_{ij} \frac{1}{R_{ij}} + H_{so} \qquad (1)$$

P_A, P_B, P_i désignent les opérateurs impulsions des noyaux A et B et des électrons i; m_A, Z_A, m_B, Z_B désignent respectivement les masses et charges des noyaux A et B et, d'une façon générale, $R_{\alpha\beta}$ représente la distance entre les particules α et β .Enfin l'intéraction spin-orbite, H_{so},désigne l'ensemble des effets relativistes.

En choisissant un nouveau système de coordonnées $\overrightarrow{R_{CM}}$, $\overrightarrow{R}$, $\overrightarrow{r_i}$ (désignant respectivement les vecteurs : position du centre de masse des noyaux ($\overrightarrow{R_{CM}}$), axe internucléaire ($\overrightarrow{R}$) et position de l'électron i par rapport au centre de masse des noyaux ($\overrightarrow{r_i}$)) la partie énergie cinétique des noyaux devient :

$$- \frac{1}{2(m_A + m_B)} \nabla^2_{R_{CM}} - \frac{1}{2\mu} \nabla^2_R - \frac{1}{2(m_A + m_B)} \sum_{i,j} \vec{\nabla}_{r_i} \cdot \vec{\nabla}_{r_j}$$

$$- \frac{1}{m_A + m_B} \vec{\nabla}_{R_{CM}} \cdot \sum_i \vec{\nabla}_{r_i} \qquad (2)$$

où $\mu = \dfrac{m_A \, m_B}{m_A + m_B}$ désigne la masse réduite des noyaux.

Dans le trièdre fixe ayant pour origine le centre de masse des noyaux et des directions quelconques, le premier et le dernier terme de (2) disparaissent.

En fait, par commodité, les coordonnées des électrons ne sont habituellement pas repérées par rapport à un trièdre fixe quelconque ayant pour origine le centre de masse des noyaux comme c'est le cas dans (2), mais par rapport à un trièdre mobile en rotation avec l'axe internucléaire.

On obtient ainsi (voir par exemple réf. /43/) :

$$\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} + \frac{1}{R^2} \left\{ (\sin\theta)^{-1} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right) + (\sin^2\theta)^{-1} \left[\frac{\partial}{\partial\phi} - i \cos\theta \, J_z \right]^2 \right\}$$

$$- \frac{1}{R^2} \left\{ \frac{J^+J^- + J^-J^+}{2} - J^+Q^+ - J^-Q^- \right\} \qquad (3)$$

avec $Q^{\pm} = \left[\mp \dfrac{\partial}{\partial\theta} + \dfrac{i}{\sin\theta} \dfrac{\partial}{\partial\phi} + \operatorname{cotg}\theta \, J_z \right]$

θ et ϕ désignent les angles d'Euler repérant le système mobile par rapport au système fixe. Le moment cinétique électronique total (J) apparaît dans (3) par sa projection J_z sur l'axe internucléaire et par ses opérateurs "d'abaissement" et "d'élévation" ($J^{\mp}$).

En regroupant les relations (1) (2) et (3), on obtient l'expression de l'hamiltonien H, exprimé dans le système de coordonnées en rotation avec l'axe internucléaire :

$$H = T_N - \frac{1}{2\mu R^2}\left[-2i\, J_z \frac{\cot g\theta}{\sin\theta}\frac{\partial}{\partial\phi} - \cot g^2\theta J_z^2\right]$$

$$+ \frac{1}{2\mu R^2}\left[\frac{J^+J^- + J^-J^+}{2} - J^+Q^+ - J^-Q^-\right] + H_{el} + H_{so} \qquad (4)$$

$$- \frac{1}{2(m_A + m_B)} \sum_{i,j} \vec{\nabla}_{r_i} \cdot \vec{\nabla}_{r_j}$$

où H_{el} désigne l'hamiltonien électronique, incluant la répulsion coulombienne des noyaux, et :

$$T_N = -\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right] - \frac{1}{2\mu R^2}\left[\cot g\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

1.2 - Equations couplées pour le mouvement des noyaux

Si l'on connaît, pour chaque distance internucléaire R, une base complète de fonctions électroniques $f_n(\vec{r}, R)$, la fonction totale du système peut être cherchée sous la forme d'un développement sur cette base

$$\Psi(\vec{r}, \vec{R}) = \sum_n C_n(\vec{R})\ f_n(\vec{r}, R) \qquad (5)$$

où $\vec{r}$ désigne globalement la position des électrons.

Cette expression doit satisfaire à l'équation de Schrödinger :

$$H|\Psi\rangle = W|\Psi\rangle$$

où W désigne l'énergie totale du système.

En utilisant l'expression (5) et en multipliant par f_p, on obtient, après intégration sur les coordonnées électroniques $\vec{r}$, le système d'équations couplées pour le mouvement des noyaux. Les fonctions f_n $(\vec{r}, R)$ de l'expression (5) ne seront pas en général les fonctions propres de H_{el} ; on les cherchera toutefois comme des représentations irréductibles du groupe de symétrie ($C_{\infty v}$ ou $D_{\infty h}$) de la molécule diatomique. Elles auront donc la symétrie Σ, Π, Δ .... suivant la valeur $\Lambda = 0, \pm 1, \pm 2$ ... de la projection, sur l'axe internucléaire, du moment orbital électronique total. L'expression des équations couplées se simplifie alors quelque peu, certains éléments étant nuls par raison de symétrie.

Si l'on se limite à des états caractérisés par une projection nulle du moment électronique total sur l'axe internucléaire, ce qui sera pratiquement toujours le cas ici, on obtient :

$$\left\{T_N + \langle f_p \mid H_{el} + H_{so} \mid f_p\rangle - \frac{1}{2\mu}\langle f_p \mid \frac{\partial^2}{\partial R^2} \mid f_p\rangle - W\right\} C_p =$$

$$-\sum_{n\neq p} \left\{ \langle f_p \mid T_N \mid f_n\rangle - \frac{1}{\mu}\langle f_p \mid \frac{\partial}{\partial R} \mid f_n\rangle \frac{\partial}{\partial R} + \langle f_p \mid H_{el} + H_{so} \mid f_n\rangle \right\} C_n \qquad (6)$$

Les simplifications proviennent de la disparition des termes dus à J_z, J^+Q^+, J^-Q^- (cf aussi note page suivante).

La relation (6) fait apparaître des termes de couplage dans le membre de droite, qui sont dus à l'hamiltonien électronique (et à l'opérateur spin-orbite) et au mouvement radial des noyaux. Ce sont les termes en $\frac{\partial}{\partial R}$ et $\frac{\partial^2}{\partial R^2}$.

Les termes de couplage radial en $\frac{\partial}{\partial R}$ sont, contrairement aux termes en $\frac{\partial^2}{\partial R^2}$, pondérés par la vitesse radiale: $\frac{1}{\mu}\frac{\partial}{\partial R}c_n$ (cf équ. 6).

Ils peuvent donc devenir importants pour des collisions à grande énergie.

L'importance relative des termes de couplage en $\frac{\partial}{\partial R}$ et $\frac{\partial^2}{\partial R^2}$ a été testée par Durup /44/ dans le cas de l'échange de charge quasi-résonnant dans la collision $H^+ + Xe$. Les termes en $\frac{\partial^2}{\partial R^2}$ n'ont qu'un petit effet sur les sections efficaces d'échange de charge pour une énergie de collision très petite (0,18 eV) et deviennent sans effet à 18 eV.

Dans le domaine énergétique considéré ici, typiquement quelques centaines d'eV, nous négligeons les termes en $\frac{\partial^2}{\partial R^2}$.*

Quand tous les couplages énoncés ci-dessus sont négligeables, l'équation (6) devient :

$$\left\{ T_N + \langle f_p \mid H_{el} + H_{so} \mid f_p \rangle - W \right\} c_p = 0$$

L'énergie électronique (et spin-orbite) joue le rôle de potentiel pour le mouvement des noyaux. Par la suite, même quand les couplages ne seront plus négligeables, on conviendra d'appeler, par extension, courbe d'énergie potentielle, la courbe $\langle f_p \mid H_{el} + H_{so} \mid f_p \rangle$ fonction de R.

Le système d'équations couplées défini en (6) n'est pas le plus général puisqu'il n'est valable, nous l'avons vu, que si l'on se limite à une base d'états caractérisés par $\Lambda = 0$ (respectivement $\Omega^{**} = 0$ dans le cas d'une intéraction spin-orbite non négligeable). Ceci exclut donc la présence de tout couplage induit par le mouvement de rotation des noyaux (cf chapitre III), mais il est néanmoins suffisant pour le bref rappel de la notion d'états adiabatiques et diabatiques présenté ci-dessous.

---

*Dans l'équation (6) ont été omis les termes $J^+J^- + J^-J^+$ et $\frac{1}{2(m_A + m_B)} \sum_{i,j} \vec{\nabla}_{r_i} \cdot \vec{\nabla}_{r_j}$ que l'on élimine par ce genre de considérations.

** Ω désigne la valeur de la projection sur l'axe internucléaire du moment électronique total incluant le spin.

1.3 - Etats adiabatiques, diabatiques

Le système d'équations couplées (6) peut être simplifié en utilisant, entre autres deux bases particulières :

1) la base $\{f_p^a\}$, dite base adiabatique, qui diagonalise l'hamiltonien électronique (éventuellement $H_{el} + H_{so}$); dans cette base, les couplages entre états électroniques sont dus aux mouvements de noyaux,

2) la base $\{f_p^d\}$ qui annule les éléments de matrice de l'opérateur $\frac{\partial}{\partial R}$ sera dite diabatique au sens de Smith /36/. Dans cette base, les couplages sont dus à l'hamiltonien électronique, éventuellement à $H_{el} + H_{so}$. En fait, une base complète et diabatique au sens de Smith, qui diagonaliserait aussi $\frac{\partial^2}{\partial R^2}$ n'est autre qu'une base constante, par exemple atomique, centrée au centre de masse des noyaux /45/. On conçoit bien qu'avec une telle base, un très grand nombre d'équations couplées devra être mis en jeu, ne serait-ce que pour décrire les états électroniques initiaux et finals de la collision. Néanmoins, on peut construire des sous-espaces diabatiques, au sens de Smith, de dimension finie. De tels sous-espaces seront construits et utilisés pour décrire l'échange de charge quasi-résonnant dans les collisions $H^+ - Xe$ et $H^+ - Kr$ (cf chapitres VII à IX).

Il sera par la suite sous-entendu que par états diabatiques, nous nous référons à la définition de Smith. Il convient toutefois de noter que d'autres approches, visant à obtenir les états appropriés au traitement des collisions atomiques, ont conduit à introduire des états également appelés diabatiques. Ces approches brièvement rappelées ici, sont plus détaillées dans les travaux de Sidis /46, 47/.

Les états adiabatiques satisfont à la règle de non-croisement des états de même symétrie de Wigner Von Neumann /48/. Leurs courbes d'énergie potentielle peuvent présenter des étranglements prononcés (cf par exemple réf /49/). On parle alors de croisement évité ou d'anti-croisement. Par ailleurs, le couplage radial entre deux états adiabatiques s'exprime par la relation /50/ :

$$\langle f_i^a \mid \partial/\partial R \mid f_j^a \rangle = \langle f_i^a \mid \partial H_{el}/\partial R \mid f_j^a \rangle (E_j - E_i)^{-1} \qquad (7)$$

Au voisinage d'un point de croisement évité, $E_j - E_i$ devient très petit et on obtient alors un couplage radial très important. Ce couplage peut devenir supérieur aux séparations énergétiques existant entre un certain nombre d'états adiabatiques et on peut se demander alors quelle signification accorder aux états f_i^a et f_j^a surtout si le système présente une succession de croisements évités /49/.

Afin de remédier à ces inconvénients on a donc, tout d'abord, cherché à construire des états violant la règle de non-croisement des états de même symétrie. C'est ainsi que Lichten /35/ a proposé d'utiliser les états décrits en simples configurations bâties sur des orbitales de type H_2^+.

O'Malley /51/, faisant l'analogie avec le problème des états moléculaires autoionisés qui croisent donc les états d'un continuum électronique, utilise pour décrire des états diabatiques croisant une série d'états de Rydberg, la même technique que celle développée dans le problème de l'attachement dissociatif. Nous avons retenu de ce travail l'idée d'utiliser des états de type valence-bond construits à l'aide d'orbitales atomiques projetées, ce qui assure un bon comportement de ces états à grande distance internucléaire. Cette méthode sera partiellement reprise dans le chapitre VII pour définir des sous-espaces diabatiques, au sens de Smith.

Dans une autre approche, Fano et Lichten /52/ et Barat et Lichten /12/ ont suggéré de construire des états diabatiques à partir d'orbitales moléculaires (cf paragraphe 1.4) diabatiques, de type H_2^+. L'utilisation de leurs diagrammes de corrélation entre les orbitales des atomes séparés et celles de l'atome uni, a permis d'expliquer un nombre considérable de résultats expérimentaux (cf par exemple réf /53/). Cette méthode est essentiellement applicable si les orbitales diabatiques cherchées sont, soit des orbitales de Rydberg, car on peut alors décrire le mouvement de l'électron dans le champ de deux noyaux écrantés par les électrons du coeur /54/, soit des orbitales des couches très internes pour lesquelles le champ coulombien, à deux centres, créé par les noyaux, prédomine. (cf par exemple réf. /55/)

Suivant les idées de Smith /36/ un sous-espace diabatique peut être obtenu, après calcul de la matrice $\frac{\partial}{\partial R}$ dans ce sous-espace, en cherchant les rotations qui minimisent (ou annulent) le couplage radial.

Ceci a été réalisé par Taulbjerg et Briggs /56/ qui obtiennent des orbitales diabatiques vérifiant les règles de corrélation de Barat-Lichten. Cette méthode nécessite le difficile et onéreux calcul de la matrice de l'opérateur $\frac{\partial}{\partial R}$ (cf paragraphe 1.4). Ces difficultés sont évitées dans une nouvelle approche, actuellement développée par Gauyacq /57/, consistant à chercher les rotations rendant douces plusieurs grandeurs rapidement variables dans la base adiabatique au voisinage de croisements évités.

Ces définitions et surtout ces façons de construire les états diabatiques, peuvent paraître assez disparates, on peut toutefois les réconcilier en adoptant une définition assez lâche d'un état diabatique. On définira un état diabatique comme un "bon état" de collision, valable dans un certain domaine de distances internucléaires et ayant un caractère lentement variable . Pour cela on conservera:

- un type de configuration donné, voir par exemple l'état $^2\Sigma_g^+$ corrélé à $He^+ + He$, défini par Lichten /35/;

- la symétrie quasi-u ou quasi-g pour les systèmes quasi-symétriques ;

un exemple particulièrement significatif peut être trouvé dans la référence /56/; les orbitales adiabatiques 2σ et 3σ de Ne-O présentent un croisement évité à faible distance internucléaire et échangent leur caractère quasi-u, quasi-g (cf réf. /56/ fig. 5), alors que les orbitales diabatiques conservent ce caractère* (voir aussi la réf. /58/ et le développement actuel de cette méthode par Sidis et al /59/);

- le nombre de noeuds de la fonction radiale /12, 54/ ;

- le caractère acquis en dehors des points de croisement /57/ (cette méthode consiste à geler les orbitales obtenues pour $R \neq R_c$ pour le calcul au point de croisement R_c);

- le caractère atomique ; ceci est développé dans le présent travail (cf chapitres VII et IX) ; l'état X corrélé à GR (np^6) + H^+ garde pour tout R son caractère atomique et l'état corrélé à GR^+ (np^5) + H a un caractère atomique lentement variable avec R. Un autre exemple peut être trouvé dans la construction d'états diabatiques pour l'intéraction spin-orbite (cf chapitre VII et réf. /60/).

---

*Dans une base formée d'un état gerade (g) et d'un état ungerade (u) on a : $\langle g|\partial/\partial R|u\rangle = 0$. C'est-à-dire qu'elle est diabatique au sens de Smith. On conçoit bien que, dans un système quasi-symétrique, le couplage radial entre un état quasi-g et un état quasi-u soit très faible. Les états qui conservent un caractère quasi-u ou quasi-g sont donc pratiquement diabatiques au sens de Smith.

1.4 - Notions pratiques

Il nous faut, avant d'aller plus loin, nous poser la question de l'obtention pratique d'une base suffisamment étendue d'états électroniques sur laquelle sera développée la fonction d'onde totale du système. Pour cela, nous devons être guidés dans notre choix par la nécessité et le désir de n'utiliser dans cette base qu'un petit nombre d'états. La nécessité est d'ordre économique car les temps de calcul augmentent beaucoup avec le nombre d'équations couplées à résoudre. Le désir est d'ordre scientifique , une base de petite dimension devant conduire à des interprétations physiques plus immédiates. Les états que nous devons construire doivent aussi se corréler de façon simple aux états électroniques des atomes séparés ; ceci pour permettre une description aisée des états initiaux et finals de la collision. On peut donc penser utiliser une base atomique formée du produit des orbitales des atomes séparés. Cette base présente le défaut de ne pas être orthogonale à distance finie, par suite du recouvrement des orbitales atomiques. Une version de cette approche sera employée dans les chapitres VII à IX. Plus fréquemment, nous utiliserons une base d'orbitales moléculaires que l'on obtient par la méthode Hartree-Fock /61/. Cette méthode consiste à chercher un état moléculaire ou atomique, fonction propre des opérateurs spin total et projection du spin sur l'axe internucléaire, sous la forme d'un ou éventuellement plusieurs déterminant (s) de Slater, bâti (s) sur des spin-orbitales orthonormales :

$$f_a = |\phi_1 \ldots\ldots \phi_n| \qquad (8)$$

Les spin-orbitales ϕ_i, généralement cherchées sous la forme de combinaisons linéaires d'orbitales X centrées sur les noyaux A et B :

$$\phi_i = \sum_j C_{ij}(R) \; X_j \qquad (9)$$

sont obtenues par optimisation variationnelle de f_a.

En fait, la méthode engendre plus d'orbitales moléculaires que les n nécessaires à la description de f_a. Plus précisément, elle en engendre autant que d'orbitales atomiques. Les orbitales $\phi_{n+1} \ldots \phi_{max}$, classées par ordre d'énergie croissante (définie comme la valeur moyenne de l'opérateur de Fock) sont appelées orbitales virtuelles /61/.

En remplaçant une ou plusieurs orbitales intervenant dans (8) par des orbitales virtuelles, on engendre des états excités (f_b...) et ainsi une base orthonormale d'états moléculaires appelée base d'états décrits par de simples configurations.

Le fait que les états moléculaires, définis ci-dessus, se corrèlent généralement de façon simple aux états atomiques (exception faite des cas symétriques) et que, d'autre part, les intéractions électroniques sont raisonnablement petites, explique l'attrait de cette façon d'engendrer une base.

Si, par ailleurs, on s'intéresse aux collisions entre deux atomes dans leur état fondamental, l'état moléculaire de plus basse énergie participe, à priori, au processus collisionnel. La convergence vers cet état par la méthode Hatree-Fock conduira à une bonne approximation de l'état adiabatique fondamental qui est certainement bien adapté pour décrire la collision, au moins dans un certain domaine énergétique et de distances internucléaires. Par contre, dans les collisions entre deux atomes excités, ce traitement doit avoir moins de succès ; la méthode Hatree-Fock convergeant en effet, sauf précautions exceptionnelles, vers l'état électronique de plus basse énergie pour une symétrie donnée.

En général, un sous-espace fini d'états moléculaires décrits en simple configuration, n'a, à priori, aucune raison d'être adiabatique ou diabatique, et donc:

$$\langle f_a \mid H_{el} \mid f_b \rangle \neq 0 \quad \text{et} \quad \langle f_a \mid \partial/\partial R \mid f_b \rangle \neq 0$$

On obtiendra un sous-espace d'états adiabatiques en mélangeant les configurations f_a, f_b .... de telle sorte que la matrice de H_{el} soit diagonale dans ce sous-espace. Cette opération, appelée "intéraction de configurations" (CI), nécessite le calcul préalable de termes de couplage ($\langle f_a \mid H_{el} \mid f_b \rangle$) de l'hamiltonien électronique. Ces termes sont assez facilement accessibles lors d'un calcul Hartree-Fock.

L'obtention d'un sous-espace d'états diabatiques (au sens de Smith) est, par contre, beaucoup plus délicate puisqu'elle suppose, en général, le calcul préalable de termes $\langle f_a \mid \partial/\partial R \mid f_b \rangle$. L'opérateur $\frac{\partial}{\partial R}$ agissant sur un déterminant de Slater comme un opérateur mono-électronique /62/, on pourra utiliser les règles de Slater /63/ lors du calcul de $\langle f_a \mid \partial/\partial R \mid f_b \rangle$ On obtient ainsi :

$\langle f_a \mid \partial/\partial R \mid f_b \rangle = 0$ si f_a et f_b diffèrent par au moins deux spin-orbitales (on obtient alors directement des états diabatiques).

$\langle f_a \mid \partial/\partial R \mid f_b \rangle = \langle \phi_a \mid \partial/\partial R \mid \phi_b \rangle$ si f_a et f_b diffèrent par une spin-orbitale (ϕ_a de f_a est remplacée par ϕ_b dans f_b). Le calcul de $\langle \phi_a \mid \partial/\partial R \mid \phi_b \rangle$ est très onéreux. En effet, l'examen de la relation (9) montre que $\frac{\partial}{\partial R} \mid \phi_b \rangle$ contiendra deux types de termes :

$$\sum_j \frac{dC_{bj}}{dR} \mid \chi_j \rangle \qquad \text{et} \qquad \sum_j C_{bj} \frac{\partial}{\partial R} \mid \chi_j \rangle$$

Le second terme ne pose pas de problème et peut même, si les orbitales χ_i du développement (9) sont des fonctions analytiques (par exemple des orbitales de Slater), être calculé analytiquement. Le premier terme, par contre, est problématique puisqu'il s'agit de connaître la variation avec R des coefficients du développement d'une orbitale moléculaire. Pratiquement, pour estimer ce terme, on sera amené à faire deux calculs moléculaires à deux distances très voisines (R et R + δR) pour pouvoir procéder à une dérivation numérique des coefficients C_{bj}. Ceci rend très difficile et onéreuse la détermination précise et complète du couplage radial sur l'intervalle $0 \leqslant R < \infty$. Notons aussi que le calcul de ce couplage dans une base adiabatique (obtenue pratiquement par un calcul d'intéraction de configurations) pose, outre la difficulté préalablement signalée, le problème du calcul de la variation avec R des coefficients du mélange de configurations.

On voit bien ici l'intérêt d'utiliser les états décrits par de simples configurations, lors de la recherche générale des états diabatiques.

Ceci explique le succès de la méthode proposée par Lichten /35/ pour le système $He^+ - He$. Notons ici que l'état $^2\Sigma_g^+$ décrit par la simple configuration $1s\sigma_g\ 2p\sigma_u^2$ (en notation de l'atome uni) croise un grand nombre d'états de même symétrie /35/ et de configuration générale $1s\sigma_g^2\ n\sigma_g$. Tous ces états différant de l'état $^2\Sigma_g^+$ par deux spin-orbitales, on obtient un couplage radial nul. Pour cet exemple, les définitions d'états diabatiques proposées par Lichten /35/ et Smith /36/ coïncident /46/.

2 - Méthode de résolution des équations couplées :

2.1 - Séparation des parties radiales et angulaires du mouvement des noyaux

Dans le cas d'un système d'équations couplées, écrit dans une base d'états pour lesquels $\Omega = 0$, et correspondant à la collision de deux atomes ayant initialement un moment électronique total nul, les fonctions d'ondes décrivant le mouvement des noyaux seront cherchées sous la forme d'un développement sur les polynômes de Legendre :

$$C_p(R,\theta) = \sum_{l=0}^{\infty} R^{-1} \; Y_p^l(R) \; P_l(\cos\theta) \qquad (11)$$

Dans le cas le plus général, la fonction sera développée sur la base des fonctions de la toupie symétrique ou sur celle des harmoniques sphériques (voir par exemple réf. /39, 43/). En utilisant la relation (11) on obtient, pour un sous-espace diabatique, les équations radiales couplées :

$$\left[\underset{\sim}{1}\,\frac{d^2}{dR^2} + \underset{\sim}{k}^2 - 2\mu\underset{\sim}{V}(R) - \underset{\sim}{1}\,\frac{l(l+1)}{R^2}\right] \underset{\sim}{Y}^l(R) = \underset{\sim}{0} \qquad (12)$$

où $\underset{\sim}{1}$ désigne la matrice unité, $\underset{\sim}{k}^2$ la matrice diagonale des nombres d'onde ($k = \sqrt{2\mu E}$) ; la matrice $\underset{\sim}{V}(R)$ est formée des termes d'énergie potentielle (diagonaux) et des termes de couplage (non diagonaux).

Le système d'équations (12) écrit sous cette forme, ou dans la base adiabatique correspondante, sert de point de départ aux théories semi-classiques des collisions atomiques, voir par exemple les références /39, 40, 64, 65/. Outre ces méthodes, on peut chercher à résoudre directement, et ceci de façon numérique, le système d'équations radiales couplées.

2.2 - Résolution des équations radiales couplées

Le système d'équations couplées (12), qui contient des dérivées secondes par rapport à R (et pas de dérivées premières) peut être résolu de façon numérique approchée. Nous rappellerons ici les méthodes de Numerov

et de Gordon que nous emploierons par la suite. Notons qu'il existe d'autres méthodes telles que celle de Vogelaere, Kouri, Jonhson (cf références /66, 67/).

a) méthode de Numerov /68/ :

C'est une méthode d'intégration à pas constant (h), qui permet de déterminer la solution $\underset{\sim}{Y}$ en un point donné R_{n+1} si on la connait aux deux points précédents, R_n et R_{n-1} tels que :

$$R_{n+1} - R_n = R_n - R_{n-1} = h$$

On obtient en effet, en développant jusqu'à l'ordre 6 par rapport à h, $\underset{\sim}{Y}$ et $\underset{\sim}{Y}''$, la relation :

$$\underset{\sim}{Y}_{n+1} + \underset{\sim}{Y}_{n-1} = 2\underset{\sim}{Y}_n + h^2 \underset{\sim}{Y}''_n + \frac{h^2}{12} \left[\underset{\sim}{Y}''_{n+1} + \underset{\sim}{Y}''_{n-1} - 2\underset{\sim}{Y}''_n \right] \qquad (13)$$

où $\underset{\sim}{Y}_{n+1}$, $\underset{\sim}{Y}_n$ et $\underset{\sim}{Y}_{n-1}$ désignent respectivement les matrices solutions aux points R_{n+1}, R_n et R_{n-1} et $\underset{\sim}{Y}'' = \frac{d^2 Y}{d R^2}$

En écrivant que $\underset{\sim}{Y}$ vérifie l'équation (12), on arrive, en posant :

$$\underset{\sim}{G} = \underset{\sim}{k}^2 - 2\mu \underset{\sim}{V}(R) - \underset{\sim}{1} \frac{\ell(\ell+1)}{R^2} \qquad (14)$$

à :

$$\underset{\sim}{Y}_{n+1} = \left(1 - \frac{h^2}{12} \underset{\sim}{G}_{n+1}\right)^{-1} \left[\left(2 + \frac{5}{6} h^2 \underset{\sim}{G}_n\right) \underset{\sim}{Y}_n - \left(1 - \frac{h^2}{12} \underset{\sim}{G}_{n-1}\right) \underset{\sim}{Y}_{n-1} \right] \qquad (15)$$

où $\underset{\sim}{G}_{n+1}$, $\underset{\sim}{G}_n$, $\underset{\sim}{G}_{n-1}$, désignent respectivement les valeurs de la matrice $\underset{\sim}{G}$ (connue) aux points R_{n+1}, R_n et R_{n-1}.

Dès lors, si l'on sait se donner deux valeurs consécutives de la matrice $\underset{\sim}{Y}$, en d'autres termes, si l'on sait amorcer l'intégration, on obtiendra $\underset{\sim}{Y}$ en tout point, en utilisant la relation (15).

Notons qu'une autre version de l'algorithme de Numerov peut être utilisée dans le cas d'un système d'équations couplées écrit dans une base non diabatique /69/. L'erreur propagée est alors plus importante et la relation entre $\underset{\sim}{Y}_{n+1}$, $\underset{\sim}{Y}_n$ et $\underset{\sim}{Y}_{n-1}$ plus compliquée. L'algorithme de Numerov ainsi adapté à l'usage d'une base adiabatique, a été utilisé par Evans et al /70/ pour prouver numériquement la coïncidence des résultats obtenus dans une base diabatique et dans la base adiabatique correspondante.

b) méthode de Gordon /42/:

On sait que les solutions $\underset{\sim}{Y}$ du système d'équations (8) sont des fonctions rapidement oscillantes avec la distance internucléaire. On peut caractériser grossièrement par une longueur d'onde locale $\lambda(R) = 2\pi/k(R)$ où $k(R)$ désigne l'impulsion radiale locale. Le pas d'intégration h intervenant dans la méthode de Numerov devra donc être choisi suffisamment petit pour que la solution calculée "suive" ces oscillations rapides. La méthode de Gordon évite cette difficulté. Elle consiste, très schématiquement, à traiter de façon analytique la partie rapidement variable de $\underset{\sim}{Y}$, pour n'intégrer numériquement que des fonctions lentement variables avec R. Nous présenterons tout d'abord la méthode de Gordon, appliquée au cas de la diffusion par un potentiel. L'équation différentielle est intégrée successivement sur des petits domaines de distances internucléaires où le potentiel est développé en série de Taylor. Dans un domaine donné, la solution générale correspondant à un développement au premier ordre du potentiel (approximation du potentiel linéaire) s'exprime comme une combinaison linéaire, indépendante de R, de fonctions d'Airy. L'écart entre le potentiel réel et l'approximation linéaire rend lentement variables les coefficients de cette combinaison linéaire. Les variations de ces coefficients, sur l'intervalle considéré, sont calculées en utilisant les relations établies par Gordon. Dès lors, la méthode se généralise à des systèmes d'équations couplées de la façon suivante .

On diagonalise la matrice potentiel au centre R_o de chaque intervalle. Les variations des coefficients du développement sur les fonctions d'Airy ne sont plus alors uniquement dues à l'écart des potentiels par rapport à l'approximation linéaire, mais aussi aux termes de couplage qui apparaissent pour $R \neq R_o$. La longueur variable de chaque intervalle est déterminée par la précision souhaitée sur la fonction d'onde. La propagation des solutions se fait en assurant la continuité des fonctions et de leurs dérivées premières aux bornes de chaque intervalle.

2.3 - Matrice de diffusion

A grande distance internucléaire, où les potentiels et les couplages s'annulent, les solutions s'expriment en terme de combinaisons linéaires des fonctions : $k_i R \; j_\ell(k_i R)$ et $k_i R \; \eta_\ell(k_i R)$ où j_ℓ et η_ℓ désignent respectivement les fonctions de Bessel et de Neuman ; k_i est le nombre d'onde sur la voie i : $k_i = \sqrt{2\mu E_i}$ (cf par exemple réf. /71/). Les coefficients du développement s'obtiennent par identification des solutions numériques aux fonctions $k_i R \; j_\ell(k_i R)$ et $k_i R \; \eta_\ell(k_i R)$.

La forme asymptotique des solutions, correspondant à un problème de collision où la voie d'entrée est repérée par i, s'exprime par les combinaisons particulières /71/ :

$$f_\ell^i(R) \underset{R\to\infty}{\sim} k_i^{1/2} \left((k_i R)\, j_\ell(k_i R) - R_{ii}^\ell \, (k_i R)\, \eta_\ell(k_i R) \right)$$

$$f_\ell^j(R) \underset{R\to\infty}{\sim} - k_j^{1/2} \, (k_j R)\, \eta_\ell(k_j R)\, R_{ij}^\ell \qquad (16)$$

qui font apparaître les éléments de la matrice réactance $\underset{\sim}{R}$.
Pour obtenir des solutions qui s'expriment sous la forme particulière (16), on est amené à résoudre n fois le système d'équations couplées de dimension n, et à chercher les combinaisons de ces solutions qui font apparaître la matrice $\underset{\sim}{R}$.

On obtient ensuite la matrice de diffusion $\underset{\sim}{S}^{\ell}$:

$$\underset{\sim}{S}^{\ell} = (\underset{\sim}{1} + i\,\underset{\sim}{R}^{\ell})\ (\underset{\sim}{1} - i\,\underset{\sim}{R}^{\ell})^{-1}$$

et enfin la section efficace différentielle :

$$\sigma_{i\to j}(\theta) = \frac{1}{4\,k_i^2}\left|\sum_{\ell=o}^{\infty}(2\ell+1)\,P_{\ell}(\cos\theta)\ (S_{ij}^{\ell} - \delta_{ij})\right|^2$$

où δ_{ij} désigne le symbole de Kronecker.

Une des difficultés inhérentes aux traitements quantiques des collisions atomiques provient du fait qu'il faut intégrer n fois le système de dimension n et obtenir des solutions linéairement indépendantes.
Le système d'équation est intégré à partir de R = O où les solutions cherchées sont nulles.* Les fonctions correspondant à des états découplés ont un comportement exponentiellement décroissant dans les régions classiquement interdites et la fonction est d'autant plus petite qu'elle correspond à une plus grande pénétration à l'intérieur de la barrière de potentiel. Si l'on intègre les équations couplées à partir d'une valeur de R suffisamment à l'intérieur des régions classiquement interdites, la valeur de la fonction qui correspond à la plus grande pénétration dans la barrière de potentiel, va rapidement devenir très grande et donc imposer sa variation, par l'intermédiaire des couplages, aux autres fonctions, et ceci quelles que soient les conditions initiales de l'intégration. On conçoit alors que des solutions linéairement indépendantes à R petit vont devenir quasi-linéairement dépendantes. Pour éviter ces problèmes on a recours à des artifices. Ainsi, dans la méthode de Numerov on annule certains couplages dans les régions classiquement interdites /41, 72/.

Nous avons écrit un programme utilisant l'algorithme de Numerov, suivant les prescriptions de Lane et Geltman /41/. D'autre part, le programme de Gordon, adapté aux problèmés de collisions atomiques par Stern et al, /73/, a été mis à notre disposition par ces auteurs.

---

* Dans les traitements semi-classiques, la séparation des ondes entrantes et sortantes permet d'imposer les conditions initiales à R = ∞. Il suffit donc d'intégrer une fois le système d'équations couplées, si l'on se contente d'une colonne de la matrice $\underset{\sim}{S}$.

La bonne marche du programme de Numerov a été essentiellement testée par comparaison aux solutions analytiques que l'on sait obtenir dans le cas de deux potentiels en "marche d'escalier" couplés par une interaction de même forme /74/. Nous avons ainsi retrouvé les critères d'intégration de Lane et Geltman /41/. Le test le plus intéressant demeure néanmoins la résolution d'un problème physique. Nous avons choisi d'étudier le processus :

$$H^+ + H(1s) \longrightarrow H^+ + H(2p)$$

pour lequel les courbes de potentiel sont bien connues et qui a été intensivement étudié (cf chapitre III).

Nous avons constaté que la méthode de Gordon est beaucoup plus rapide que celle de Numerov, surtout quand l'énergie de la collision est élevée. Ceci est dû au fait que le pas d'intégration dans la méthode de Gordon dépend assez peu de l'énergie /42/, contrairement à ce qui se passe dans la méthode de Numerov où l'on retient habituellement $h = \frac{\lambda_\infty}{20}$ (λ_∞ étant la plus petite des longueurs d'onde associées au mouvement des noyaux, quand $R \longrightarrow \infty$). En fait, on peut augmenter le pas d'intégration dans la méthode de Numerov si l'on se contente d'une précision modeste sur la fonction d'onde, cependant, un pas d'intégration supérieur à $\frac{\lambda_\infty}{10}$ semble déraisonnable /42/. La méthode de Gordon nous a permis de traiter quantiquement les équations couplées dans des cas qui paraissaient inaccessibles (car trop onéreux) avec le programme de Numerov (par exemple, la résolution de 2000 ondes partielles d'un système de quatre équations couplées à une énergie de collision de 200 eV).

Chapitre III

ETUDE DU SYSTEME COLLISIONNEL $H^+ - H$

Importance du couplage rotationnel

Le système $H^+ - H$, le plus simple des systèmes collisionnels, pour lequel on connaît bien les courbes de potentiel, a bénéficié d'une étude théorique importante et sert généralement de test aux nouveaux formalismes de la physique des collisions.

Depuis le travail de Bates et Williams /75/ on sait que le processus d'excitation essentiel dans les collisions $H^+ - H$ est dû au couplage rotationnel entre les états $2p\sigma_u$ et $2p\pi_u$ dégénérés à R nul. La transition électronique provient de l'effet de la rotation des noyaux sur la fonction d'onde électronique, l'électron ne parvenant pas à suivre, adiabatiquement, la rotation de l'axe internucléaire qui repère la symétrie de son orbitale et sur lequel est projeté son moment orbital.

L'intérêt de l'étude du couplage rotationnel $2p\sigma_u - 2p\pi_u$ provient du fait que ce mécanisme est souvent responsable des processus d'excitation importants dans la physique des collisions. C'est lui qui permet d'expliquer certains processus d'excitation des électrons de valence (cf par exemple les systèmes He - He, He^+ - He, Li^+ - He /76/) et c'est aussi le processus prépondérant d'excitation en couche interne K /77/ pour les systèmes symétriques (cf par exemple les systèmes $C^+ - C$, $N^+ - N$, $O^+ - O$, $Ne^+ - Ne$ /78/) ainsi que pour les systèmes dissymétriques /79/. Ceci explique l'effort voué par les spécialistes des collisions à haute énergie à l'étude du couplage rotationnel, afin d'obtenir des lois universerselles pour les probabilités et les sections efficaces d'excitation des couches internes /80/.

Differential cross section from quantal solutions for excitation of H into 2p state in H^+–H collisions*

C Kubach† and V Sidis‡§

† Laboratoire des Collisions Ioniques, Université de Paris-Sud, 91405 Orsay, France
‡ Centre de Mécanique Ondulatoire Appliquée, 23 rue du Maroc, 75019 Paris, France

Received 9 July 1974

Abstract. We report on the calculation of the differential cross section for excitation of the 2p state of H in H^+–H collisions at an energy of 205 eV(CM). The computational method consists in solving, using the Numerov algorithm, the set of quantal two-state close-coupled equations relative to the $2p\sigma_u$ and $2p\pi_u$ molecular states of H_2^+ in the perturbed stationary state approximation (Mott 1931). Comparison is made with the experimental data of Houver *et al* (1974) together with results of the common trajectory method of Gaussorgues *et al* (1974). The efficiency of the latter method is confirmed.

Since the work of Bates and Williams (1964) an abundant literature on the study of H^+–H collisions has well established that rotational coupling between the $2p\sigma_u$ and $2p\pi_u$ states of H_2^+ is the dominant mechanism for inelastic processes which are actually almost exclusively confined to the excitation of the $n = 2$ levels of H (Houver *et al* 1974). As argued by Knudson and Thorson (1970) and verified by Chidichimo-Franck and Piacentini (1974) couplings between the entrance channel $2p\sigma_u$ and states higher than $2p\pi_u$ (Rosenthal 1971) are not efficient in inducing transitions at moderate collision energies; this justifies a two-state truncation for dealing with inelastic processes in this system. To our knowledge, all the calculations undertaken for studying these processes have been carried out in semi-classical or semi-quantal frameworks such as the impact parameter method (IPM) of McCarroll and Piacentini (1970) and Gaussorgues and Salin (1971), the eikonal approximation of Chen *et al* (1972), the mixed JWKB-quantal treatment of Knudson and Thorson (1970) and the common trajectory method (CTM) of Knudson and Thorson (1970) and Gaussorgues *et al* (1974). We present here the results of a direct numerical integration of the two-state close-coupled second-order differential equations relative to the $2p\sigma_u$ and $2p\pi_u$ molecular states of the H^+–H system in the perturbed stationary state approximation (we thus neglect translational factors as those discussed earlier by Bates and Williams 1964, Thorson 1965, Bates and Sprevak 1971). The aim of this work is twofold: it intends to put in evidence additional quantal effects, if any, which may arise from an eventual departure from the semi-classical assumptions (JWKB approximation, separation of ingoing and outgoing waves, neglection of couplings in the non-classical region, validity of the common trajectory choices) and to look for the feasibility of numerical quantal calculation in problems such as rotational coupling near the united atom limit for which it is expected that the contribution to the inelastic cross section will only arise from a relatively small number of partial waves.

§ Present address: Laboratoire des Collisions Atomiques, Université de Paris-Sud, 91405 Orsay, France.

* J. Phys. B: Atom. Molec. Phys., Vol. 8, No. 4, 1975. Printed in Great Britain. © 1975

As in a previous work (Kubach *et al* 1974) the Numerov algorithm was used to integrate for each angular momentum the second-order differential equations obtained by expanding the total wavefunction over partial waves in a way similar to that described by Knudson and Thorson (see equations (1) to (10) of their paper). The resulting scattering matrix elements are involved in a summation over Legendre polynomials in the usual way. This evaluation of the scattering amplitude for a Σ–Π transition implies that the projection of the total angular momentum of the system on the internuclear axis is not conserved. The validity of this approximation has already been discussed by Knudson and Thorson (1970) and by Gaussorgues *et al* (1974) and need not be repeated here. Details of the numerical procedure have been given elsewhere (Evans *et al* 1972, Kubach *et al* 1974). The potential energy curves for the $2p\sigma_u$ and $2p\pi_u$ states of H_2^+ were taken from Bates and Reid (1968) and the rotational coupling matrix elements $\langle Ly \rangle$ were those computed by Salin (see Gaussorgues *et al* 1974). For the sake of convenience these potentials and couplings were represented by analytical fits having an accuracy of about 1 %. The coupled equations were integrated up to an internuclear distance of 13 Bohr and the cross sections were evaluated with 280, 750, 880 and 1100 partial waves.

The transition probability plotted in figure 1 as a function of l, for a collision energy of 205 eV (CM), shows good agreement with the CTM results and confirms the defect of the IP method (broken curve) especially at small values of l. Differential cross sections

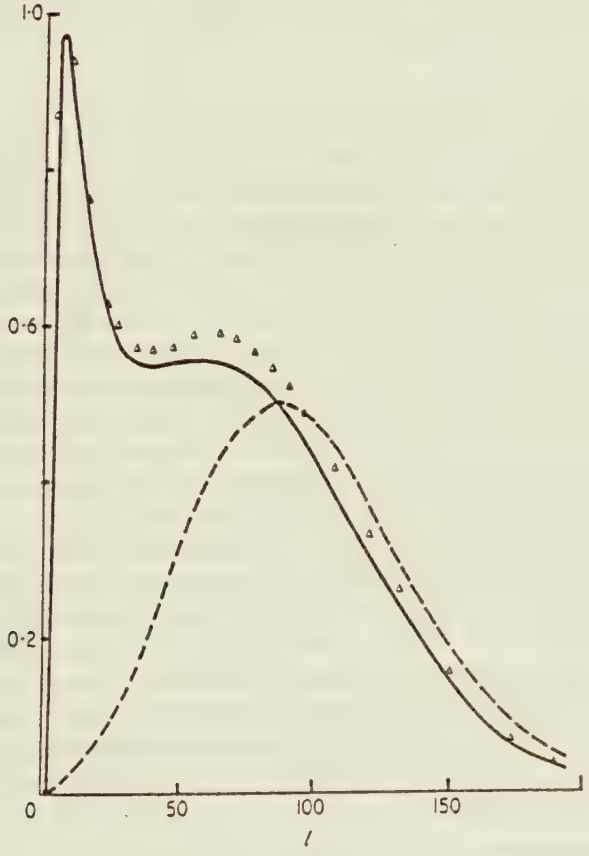


Figure 1. Excitation probability as a function of l. —— Quantal result (present work), – – – IPM (Gaussorgues *et al* 1974), △ CTM (Gaussorgues *et al* 1974).

for direct excitation of H into the 2p state are shown in figure 2. The present results differ from the CTM ones of Gaussorgues *et al* (1974) by 4 to 8%. This discrepancy arises from the different interpolation methods for the potentials and couplings used in that work. Indeed CTM calculations have subsequently been performed by Masnou-Seeuws (1974 private communication) using our fits†, and the resulting cross section, also plotted on figure 2, shows improved agreement with ours. As expected the IP method

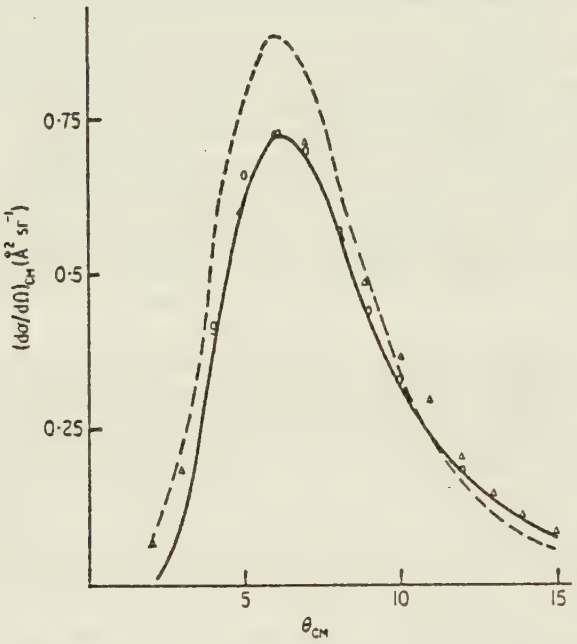


Figure 2. Differential cross section (in Å^2 sr^{-1}) for direct excitation into the 2p state. —— Present work, – – – IPM (Gaussorgues *et al* 1974), △ CTM (Gaussorgues *et al* 1974), ○ CTM with our analytically fitted potentials and coupling (Masnou-Seeuws 1974 private communication).

gives relatively poor results at larger angles. The comparison of the present results with the experimental data of Houver *et al* (1974) (figure 3) although satisfactory still shows a sensible discrepancy especially at small angles where the experimental cross sections are most affected by corrections accounting for apparatus effects. Elastic and resonant charge exchange cross sections have not been computed because they would require larger numbers of partial waves and computing times.

A special feature observed in our calculation which deserves attention is that inelastic cross sections evaluated with an increasing number of partial waves stabilize around eg $l = 280$ for θ (CM) $\geqslant 5$ degrees showing, as expected, that large impact parameters do not contribute to large scattering angles. However, at small angles (around zero degrees) the inclusion of additional hundreds of partial waves generates a peak which grows up to a value ten times larger than the maximum of the cross section at larger angles when $l = 1100$. Since the transition probability here should go to zero as l tends to infinity this peaking can be nothing but a spurious effect. Calculations show that this effect has two sources:

† The fit used by Gaussorgues *et al* (1974) is more accurate than ours. Thus for any comparison with experiment the best computational data are those of Gaussorgues *et al* (1974) (triangles in figure 2).

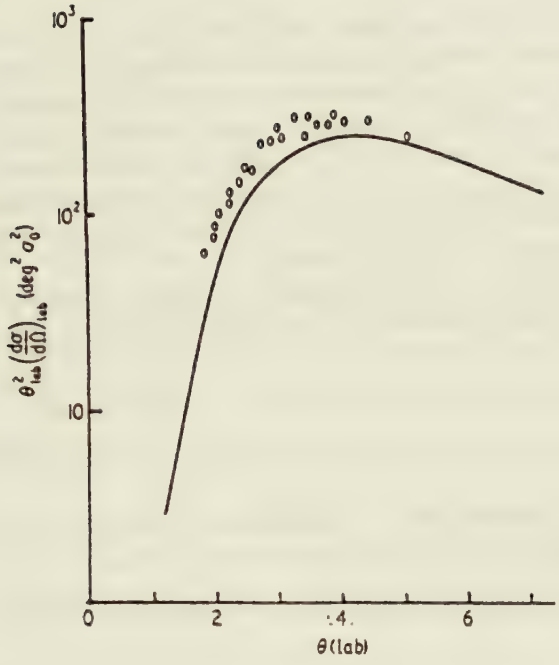


Figure 3. Reduced differential cross section $\theta^2_{lab}(d\sigma/d\Omega)_{lab}$ (θ_{lab} in degrees, $d\sigma/d\Omega$ in $a_0^2\,sr^{-1}$) for direct excitation of H into the 2p state. —— Present work, ○ experiment (Houver *et al* 1974) where the ordinate scale was calibrated according to earlier calculations.

(i) The first one is the behaviour of the $\langle Ly \rangle$ matrix element which increases as R at large internuclear distance ('long moment arm' Thorson 1965) and gives rise to a coupling which behaves as $l(l+1)/R$. As pointed out by Bates and Williams (1964), Thorson (1965), and Bates and Sprevak (1971), this behaviour is spurious and arises from the neglect of adequate translational factors in the wavefunction. This spurious coupling is usually claimed to be unimportant because the only significant region is that at small internuclear distances where the $2p\sigma_u$ and $2p\pi_u$ states become energetically close to each other (Bates and Sprevak 1971). Nevertheless, for large l this spurious coupling leads to finite (although small) scattering matrix elements which are weighted by large $(2l+1)$ factors in the scattering amplitude and thus affects the differential cross section at small angles.

(ii) The second one is the finite accuracy of the numerical integration which at large l gives small scattering matrix elements affected by large relative errors (which usually depends on the integration parameters). This background can also be enhanced in the scattering amplitude summation at small angles. This feature has probably been encountered in other works and rejected as unphysical; it shows how exact an 'exact' calculation can be.

The good agreement between the present calculation and the CTM one shows that no noticeable additional quantal effects can be detected in this case at moderate energies. This comparison confirms the efficiency of the CT method (for cases in which a common trajectory can be adequately chosen) in regard to its accuracy and economic time consumption. We have observed that quantal cross sections require total computing times twice as large as those needed to achieve the CTM calculation. Nevertheless the time necessary to solve the set of coupled equations for a single partial wave is much

smaller in the direct numerical resolution used here than in the numerical iterative resolution of the first-order differential equations involved in the CT method. The differences between total computing times arise from the factorization in CTM of the rapidly oscillating terms out of the scattering matrix elements, which allows the use of interpolation methods on the remaining factor and thus reduces the number of partial waves to be worked on. Such interpolating procedures along with efficient integration methods should be looked for if numerical resolutions are wanted to compete with semi-classical methods.

This work initiates a programme of comparison between quantal and CTM calculations in cases where the latter is expected to have less complete success (Knudson and Thorson 1970).

Acknowledgments

We wish to thank Drs F Masnou-Seeuws, C Lesech and C Gaussorgues for stimulating collaboration and communication of results prior to publication.

References

Bates D R and Reid R H B 1968 *Adv. Atom. Molec. Phys.* **4** 13–35
Bates D R and Sprevak D 1971 *J. Phys.* B: *Atom. Molec. Phys.* **4** L47–51
Bates D R and Williams D A 1964 *Proc. Phys. Soc.* **83** 425–33
Chen J C Y, Ishihara T, Ponce V H and Watson K M 1972 *J. Phys.* B: *Atom. Molec. Phys.* **5** L204–6
Chidichimo-Franck M G and Piacentini D R 1974 *J. Phys.* B: *Atom. Molec. Phys.* **7** 548–57
Evans S A, Cohen T S and Lane N F 1971 *Phys. Rev.* A **4** 2235–48
Gaussorgues C, Lesech C, Masnou-Seeuws F, McCarrol R and Riera A 1975 *J. Phys.* B: *Atom. Molec. Phys.* **8** 239–52, 253–64
Gaussorgues C and Salin A 1971 *J. Phys.* B: *Atom. Molec. Phys.* **4** 503–12
Houver J C, Fayeton J and Barat M 1974 *J. Phys.* B: *Atom. Molec. Phys.* **7** 1358–69
Knudson S K and Thorson N R 1970 *Can. J. Phys.* **48** 313–29
Kubach C, Sidis V and Durup J 1975 *J. Phys.* B: *Atom. Molec. Phys.* **8** to be published
McCarrol R and Piacentini R D 1970 *J. Phys.* B: *Atom. Molec. Phys.* **3** 1336–45
Mott N F 1931 *Proc. Phil. Soc.* **27** 553–60
Rosenthal H 1971 *Proc. 7th Conf. on Physics of Electronic and Atomic Collisions* (Amsterdam: North-Holland) pp 105–7
Thorson W R 1965 *J. Chem. Phys.* **42** 3878–91

DISCUSSION ET COMMENTAIRES

1 - Les transitions dues au couplage rotationnel interviennent essentiellement à petites distances internucléaires. On constate en effet (cf fig. 1) que la probabilité d'excitation devient extrêmement faible pour $\ell > 200$, c'est-à-dire pour des paramètres d'impact supérieurs à 1,7. Ceci signifie que, pour des distances internucléaires supérieures à cette valeur, le système évolue adiabatiquement sur la voie $2p\sigma_u$.

2 - Signification du pic étroit observé aux petits paramètres d'impact.

La figure 1 montre la présence d'un pic étroit correspondant à une probabilité proche de 100 % pour ℓ voisin de 8. Ce pic, n'apparaissant pas dans le traitement en paramètre d'impact de la collision (fig.1), doit être rattaché à un effet de trajectoire. Semi-classiquement, on s'attend à avoir une probabilité d'excitation très grande pour un angle de diffusion de 90° dans le système du centre de masse. En effet, considérons une orbitale $2p_z$ repérée par rapport à un axe "nucléaire" coïncidant initialement avec z, cette orbitale est appelée $2p\sigma$. Si l'on fait tourner très rapidement de 90° l'axe de référence, cette même orbitale est devenue $2p\pi$. On a donc effectué la transition $2p\sigma_u \longrightarrow 2p\pi_u$ par couplage rotationnel.

Pour connaître le paramètre d'impact correspondant à un angle de diffusion donné, il faut définir une trajectoire et donc un potentiel effectif régissant le mouvement des noyaux. A faible distance internucléaire, les courbes de potentiel des états $2p\sigma_u$ et $2p\pi_u$ ont un comportement essentiellement coulombien (en 1/R) on peut donc utiliser la loi $\theta(b)$ de la diffusion classique pour un potentiel coulombien. On obtient ainsi /81/ :

$$\theta(b) = \Pi - 2 \text{ arctg } (2 Eb)$$

où E désigne l'énergie de la collision dans le centre de masse.
L'angle $\theta = 90°$ correspond à un paramètre d'impact b_m défini par la relation :

$$b_m = 1/(2E)$$

On obtient ainsi avec E = 205 eV : $b_m = 0{,}066\ a_o$ soit $\ell_m \simeq 8$.
Plus précisément , on doit s'attendre à avoir une probabilité de transition de la forme :

$P(\theta) = \sin^2\theta$ qui représente le carré de la composante π d'une orbitale, initialement $2p\sigma$, obtenue après une rotation de θ , soit :

$$P(b) = \frac{16\,E^2.b^2}{(1 + 4\,E^2\,b^2)^2}$$

Cette relation a été obtenue par Briggs et Macek /82/.
La figure 4 montre l'excellent accord à petit paramètre d'impact entre la probabilité de transition résultant du calcul quantique et le résultat obtenu en utilisant la formule de Briggs et Macek. On conçoit bien que la méthode du paramètre d'impact, utilisant une trajectoire rectiligne, ne puisse correctement reproduire ce pic "cinématique". Au contraire, il est logique que la méthode de la trajectoire commune /83/, utilisant le potentiel de l'état $2p\sigma_u$ (coulombien à petite distance),où le potentiel 1/R,donne le bon résultat (cf fig 1).

Sur la figure 4 sont également portées les probabilités des transitions obtenues en utilisant les valeurs "universelles", tabulées par Taulbjerg et al /80/ en unités réduites, pour les deux énergies 185 et 227 eV encadrant la valeur 205 eV pour laquelle nos calculs ont été effectués.
Le bon accord observé est une preuve de la valeur du traitement de Taulbjerg et al. Notons que cet accord est amélioré si l'on utilise la probabilité de transition obtenue par Gaussorgues et al /83/ (cf fig 1). Ceci est dû au fait que ces derniers auteurs ont une description des potentiels plus précise que la nôtre.

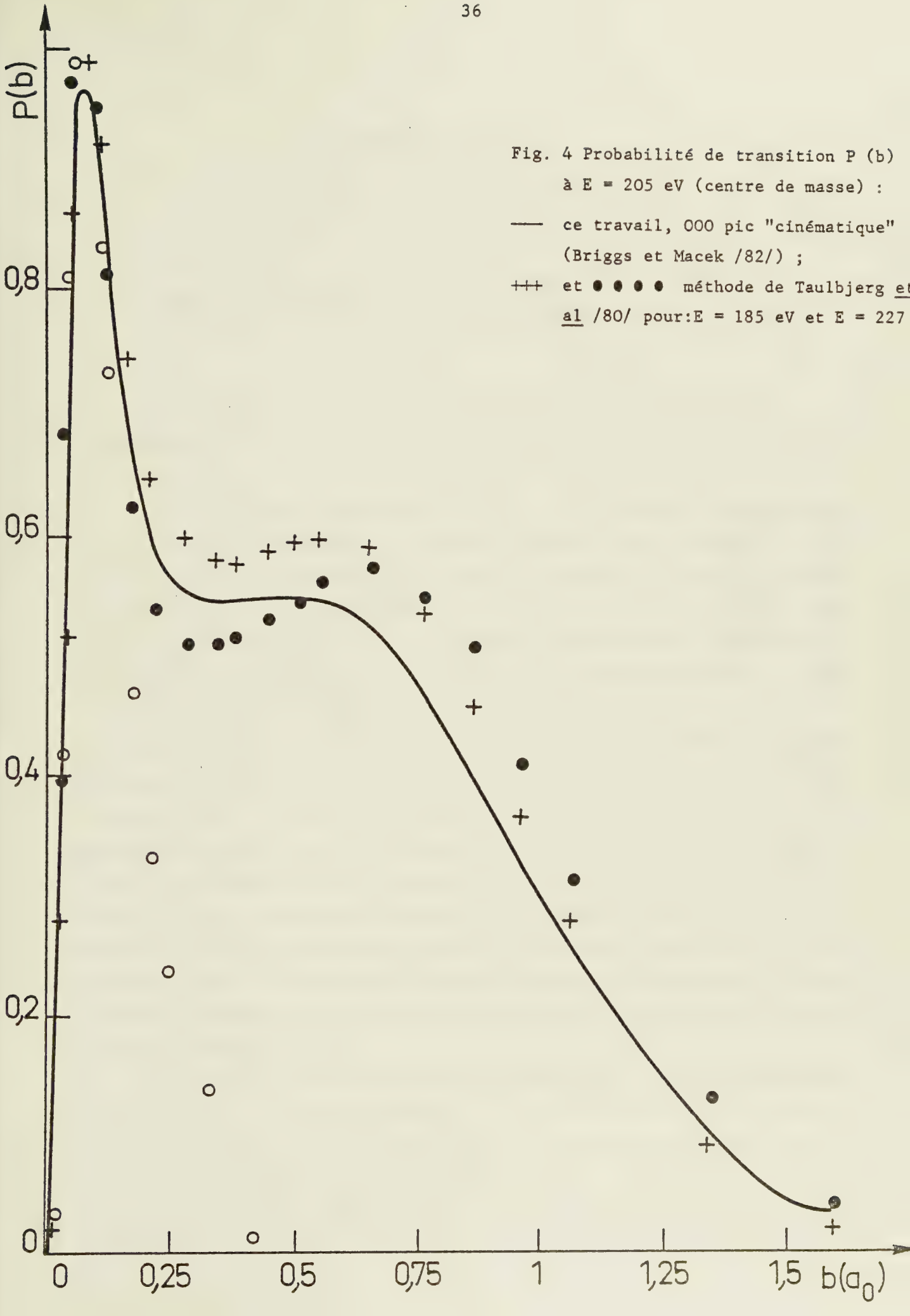


Fig. 4 Probabilité de transition P (b) à E = 205 eV (centre de masse) :

—— ce travail, OOO pic "cinématique" (Briggs et Macek /82/) ;

+++ et ● ● ● ● méthode de Taulbjerg et al /80/ pour:E = 185 eV et E = 227

Chapitre IV

ETUDE MOLECULAIRE DU SYSTEME COLLISIONNEL H^+ - Xe

Introduction

L'utilisation par Abignoli et al /11/ du modèle de corrélation des orbitales diabatiques /12/ a montré que, seul dans la série H^+ - GR, le système H^+ - Xe présente un croisement de courbes d'énergie potentielle entre les voies corrélées à $H^+ + Xe\ (5p^6)$ et $H + Xe^+\ (5p^5)$. Des transitions localisées à ce point de croisement permettraient d'expliquer le comportement oscillatoire de la probabilité d'échange de charge, en fonction de l'angle de diffusion, observé dans les collisions H^+ - Xe /11/.

En fait, l'existence de ce point de croisement permet de comprendre, à posteriori, les difficultés rencontrées par Weise et al /9/ dans l'interprétation des expériences de diffusion élastique de H^+ sur Xe. Ces auteurs montrent en effet, que l'on ne peut déterminer, à partir des mesures de sections efficaces différentielles élastiques à faible énergie dans la collision H^+ - Xe, le puits de potentiel de l'ion moléculaire $(H\text{-}Xe)^+$, alors qu'une telle opération est possible pour tous les autres systèmes H^+ - G R. Ne pouvant décrire la collision élastique à l'aide d'un potentiel unique, ils proposent un puits de potentiel "effectif", de profondeur variable avec l'énergie de collision, pour reproduire les sections efficaces mesurées.

On peut conclure des travaux de Weise et al /9/ qu'un effet perturbateur, dû à des couplages entre l'état correspondant au puits de potentiel et d'autres états électroniques, se manifeste à de très faibles énergies de collision (quelques dizaines d'eV).

On peut être tenté, connaissant les travaux d'Abignoli et al, d'attribuer un tel effet perturbateur à la présence du croisement de courbes

d'énergie potentielle discuté ci-dessus. On connaît, en effet, l'importance que revêtent les croisements entre états diabatiques, ou les croisements évités entre états adiabatiques, pour les processus élastiques et inélastiques dans les collisions atomiques (cf, par exemple, réf. /35, 84, 85/). Cette importance justifie les nombreux travaux théoriques (cf par exemple, réf. /65, 86 -89/) discutant la validité du modèle dû à Landau /90/, Zener /91/ et Stueckelberg /22/, qui permet d'estimer la probabilité de transition au point de croisement.

Il paraît donc intéressant de savoir si l'on peut vérifier, par un calcul ab-initio moléculaire, les hypothèses d'Abignoli et al /11/ mais aussi, et surtout, si l'on peut déterminer l'influence du point de croisement sur les processus élastique et d'échange de charge quasi-résonnant dans les collisions H^+ - Xe.

Potential energy curves of the $(XeH)^+$ system*

C Kubach† and V Sidis‡

†Laboratoire des Collisions Ioniques,§ Universite de Paris-Sud, 91405—Orsay, France
‡Centre de Mecanique Ondulatoire Appliquée, 23 rue du Maroc, Paris 75019

Received 13 July 1973

Abstract. *Ab initio* calculations have been carried out on some potential energy curves of the $(XeH)^+$ molecule, with particular attention paid to the lowest states. The spin–orbit interaction has been taken into account using a semi-empirical method. These calculations suggest the use of a three-state basis when dealing with H^+–Xe collisions at low energies. It is also found that the computed MO correlation diagram is in good agreement with that predicted by the 'promotion model' of Barat and Lichten (1972).

LCAO-MO-SCF calculations have been performed on some potential energy curves and wavefunctions of the $(XeH)^+$ molecule using the ALCHEMY program written by Bagus and coworkers¶. To our knowledge it is the first calculation on this system. The basis set of Slater-type orbitals used throughout the whole range of internuclear distances investigated (from 0·5 to 10 Bohrs) is given in table 1. The non-marked STO on the Xe center are slightly different from those of the minimal basis set of Clementi *et al* (1967) while new sets of 5s, 5p, 4d orbitals were optimized in preliminary calculations on the ^1S ground state of Xe and the additional 6s, 6p, 5d and 4f STO were introduced in order to allow for the calculation of molecular states dissociating into $H^+ + Xe^*$. The improvement thus obtained in the energy level of Xe ^1S with respect to the result of Clementi amounts to 4·3 Hartrees. The STO on H are those used by Peyerimhoff (1965) augmented by orbitals allowing for the description of the $n = 2$ levels of H.

Figure 1 shows the two lowest single-configuration $^1\Sigma^+$ potential energy curves arising from $(\ldots 11\sigma^2 \ldots 6\pi^4)\ X^1\Sigma^+$, and $(\ldots 11\sigma' 12\sigma' \ldots 6\pi^4)\ I^1\Sigma^+$: the equilibrium internuclear distance of XeH^+ is located at $R_e = 3{\cdot}0$ Bohr, which is very close to that of the isoelectronic system IH (3·03 Bohr, cf Herzberg 1950). The well depth of the $X^1\Sigma^+$ state is found to be $U = 0{\cdot}2129$ Hartree.

This is to be compared to the semi-experimental predictions of Weise *et al* (1971); a detailed comparison between these results will be given in a forthcoming paper concerned with cross section calculations. The predicted crossing (Weise *et al* 1971, Abignoli *et al* 1972) between $X^1\Sigma^+$ and $I^1\Sigma^+$ occurs at $R = 5{\cdot}5$ Bohr.

§ Part of the Laboratoire de Physico-Chimie des Rayonnements, associated to the CNRS

¶ P S Bagus, B Liu, A D McLean and M Yoshimine of the Theoretical Chemical Group at IBM research in San Jose, California. Preliminary descriptions of the ALCHEMY program are given by McLean in *Proc. Conf. Potential Energy Surfaces in Chemistry* (California University, Santa Cruz 1970) and by Bagus in *Selected Topics in Molecular Phys*, (Berlin 1972). See also IBM Research publication 14748 (1971).

* J. Phys. B: Atom. Molec. Phys., Vol. 6, October 1973. Printed in Great Britain. © 1973

Table 1. The basis set of STO

n	*l*	zeta	nucleus
1	0	52·9934	Xe
2	0	18·8964	Xe
3	0	10·9210	Xe
4	0	7·0380	Xe
5	0	2·8568*	Xe
5	0	8·0528*	Xe
6	0	1·1022*	Xe
2	1	24·9184	Xe
3	1	11·8683	Xe
4	1	6·3962	Xe
5	1	2·0106*	Xe
5	1	3·5389*	Xe
6	1	1·0333*	Xe
3	2	13·9136	Xe
4	2	7·5720*	Xe
4	2	4·5732*	Xe
5	2	0·5754*	Xe
4	3	0·2500*	Xe
1	0	1·1950	H
1	0	0·5000	H
2	0	1·1804	H
2	0	2·5623	H
2	0	0·5000	H
2	1	1·8451	H
2	1	0·5000	H
3	2	2·7577	H

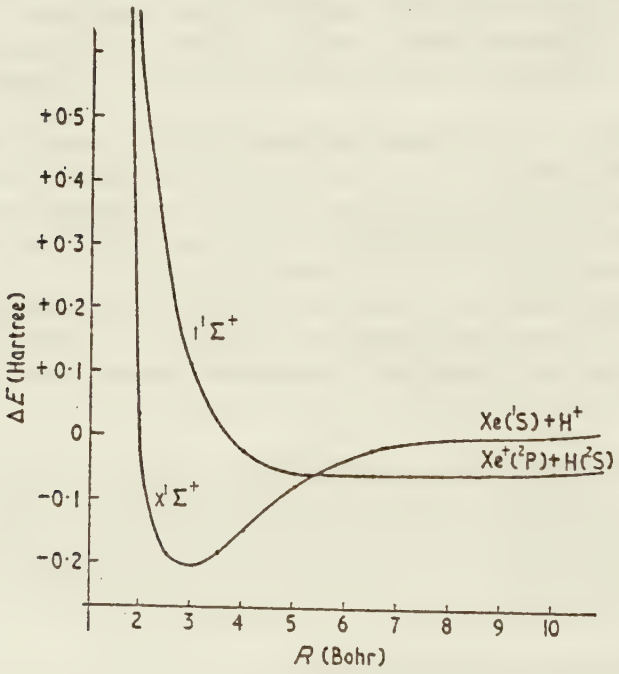


Figure 1. Two lowest potential energy curves $^1\Sigma^+$ of XeH^+. The energy of Xe is chosen as zero.

In view of calculating cross sections, the $X^1\Sigma^+$ and $I^1\Sigma^+$ states which were obtained from closed-shell and open-shell calculations, respectively, have been orthogonalized in such a way that the couplings involved between them remain small (< 3eV). The off-diagonal matrix elements involving the new orthogonal states $X^1\Sigma^+$,

$$K^1\Sigma^+ = (|I^1\Sigma^+\rangle - S|X^1\Sigma^+\rangle)/(1-S^2)^{1/2}$$

(with $S = \langle X^1\Sigma^+|I^1\Sigma^+\rangle$) and the closest states are:

(i) (H_{el}) and (H_{so}), with magnitudes of the order of 10^{-2} Hartree

(ii) $(v_0 bL_y/R^2)$, inducing a rotational coupling, which at 30 eV and at the crossing point is at most twenty times smaller than the interactions in (i),

(iii) $(v_R \partial/\partial R)$, which are expected to be small since the states $X^1\Sigma^+$ and $K^1\Sigma^+$ are built up from orbitals which change neither drastically nor suddenly, except at $R < 3$ Bohr. It is thus justified, at least at low energy, to consider only the couplings due to (i).

Since the $(XeH)^+$ system involves a heavy element it is necessary to take into account the spin–orbit interaction in the calculation of potential energy curves, for the states to have a correct dissociation limit when R tends towards infinity. This is done below for the potential curves tending to the energy levels of $H + Xe^+(^2P_{3/2})$ and $H + Xe^+(^2P_{1/2})$.

We consider here only the substates with $\Omega = 0$ ($\Omega = \Lambda + \Sigma$), which are coupled to the molecular incoming channel generated by $H^+ + Xe$, and consist of the $K^1\Sigma^+$ and the lowest $^3\Sigma$ and $^3\Pi$ states. This subspace is built up from the following $|\Omega, \Lambda, S, \Sigma\rangle$vectors : $|0, \pm 1, 1, \pm 1\rangle$, $|0, 0, 1, 0\rangle$ and $|0, 0, 0, 0\rangle$.

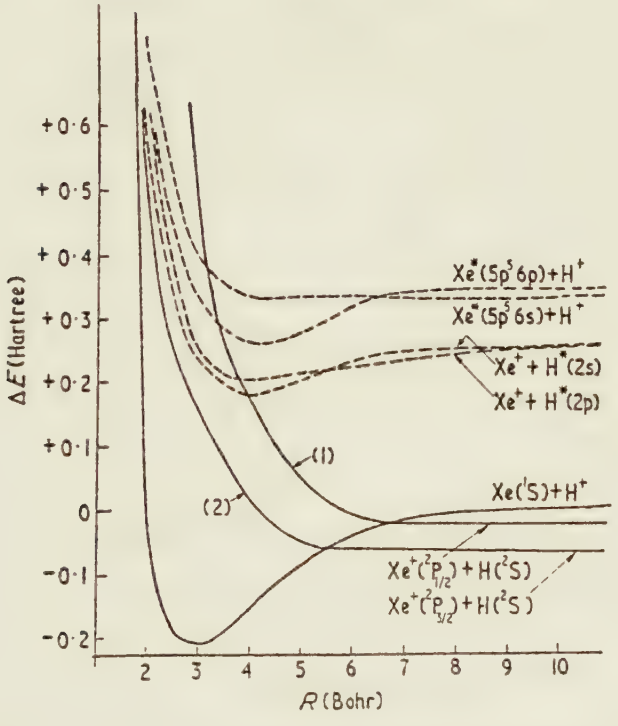


Figure 2. Some potential energy curves of XeH^+. ——— the three orthogonal states taking into account the spin–orbit interaction; – – – energy curves $^1\Sigma^+$ dissociating into $H^+ + Xe^*$ or $H(n = 2) + Xe^+$.

By making a basis change to: $\Phi\pm = (|0, +1, 1, -1> \pm |0, -1, 1, +1>)/^{1/2}$; $|0, 0, 1, 0>$, and $|0, 0, 0, 0>$, and approximating the spin orbit operator by a mono-electronic operator as in the work of Walker and Richards (1968) and that of Ishiguro and Kobori (1967) it is possible to reduce the problem to two 2×2 secular equations linking Φ^+ and $|0, 0, 1, 0>$ on one hand, and Φ^- and $|0, 0, 0, 0>$ on the other hand. The molecular integrals at large internuclear distances, where the coupled states are close to one another may be reduced in a standard way to sums of atomic integrals weighted by overlap factors. These atomic integrals were derived empirically from the experimental splitting displayed in the tables of Moore (1958). The two states diagonalizing $H_{el}+H_{so}$ in the $(\kappa^1\Sigma^+, \Phi^-)$ subspace lead to the potential energy curves (1) and (2) plotted on figure 2. These states are presently used in elastic and charge-transfer differential cross section calculations at low energy (from 15 to 60 eV).

Figure 2 also shows some excited $^1\Sigma$ potential energy curves dissociating into either $H^+ + Xe^*$ or $H(n = 2) + Xe^+$ which are obtained using the 'virtual orbital' approximation and without taking into account the relativistic effects. These curves exhibit crossings or pseudo-crossings with the curves (1) and (2) around 4 Bohrs, leading to a reduced angle $\tau = E\times\theta \simeq 0{\cdot}8$ keV . degree, which is consistent with the thresholds observed by Abignoli *et al* (1971) for the excitation and charge exchange processes.

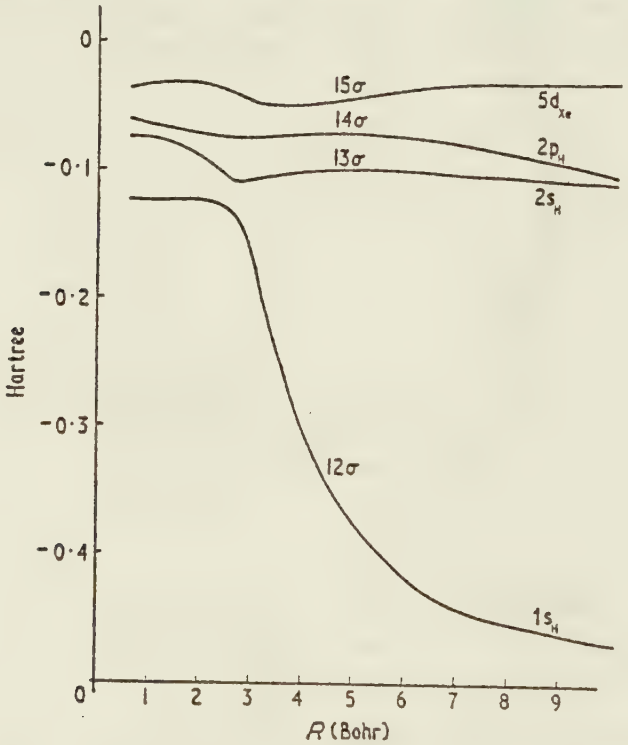


Figure 3. Computed σMO correlation diagram.

On figure 3 we have plotted the computed MO correlation diagram which shows clearly the promotion of the 12σ orbital, originally $1s_H$. Also is observed a pseudo-crossing at $R = 2{\cdot}5$ Bohr of this MO level with those issuing from $H(n = 2)$. This is

in good agreement with the correlation diagram of Abignoli *et al* (1972) obtained from the Barat and Lichten (1972) correlation rules.

The authors wish to acknowledge the assistance of D Grimbert-Cazes during the calculations.

References

Abignoli M, Barat M, Fayeton J and Hoover J C 1972 *J. Phys.* B: *Atom. molec. Phys.* **5** 1533–53
Barat M and Lichten W 1972 *Phys. Rev.* A6 211–29
Clementi E, Raimondi D L and Reinhardt W P 1967 *J. chem. Phys.* **47** 1300–7
Herzberg F R S 1950 *Molecular Spectra and Molecular Structure* (Princeton, NJ: Van Nostrand)
Ishiguro E and Kobori M 1967 *J. Phys. Soc. Japan* **22** 263–70
Moore C 1958 *Atomic Energy Levels* Vol III National Bureau of Standards 467
Peyerimhoff S 1965 *J. chem. Phys.* **43** 998–1010
Walker T E H and Richards W 1968 *Symp. Faraday Soc.* **64**
Weise H P, Mittman H P, Ding A and Henglein A 1971 *Z. Naturf.* **26a** 111221

DISCUSSION ET COMMENTAIRES

1. Les calculs moléculaires présentés ci-dessus illustrent la difficulté rencontrée pour reproduire le croisement attendu, entre les courbes de potentiel corrélées à $Xe^+ + H$ et $Xe + H^+$ /11/. Nous n'avons pu, en effet, utiliser la méthode des orbitales virtuelles /61/ puisque, dans cette approximation, l'état I se situerait toujours énergétiquement au-dessus de l'état X et aurait donc une limite de dissociation incorrecte. La méthode retenue ici consiste à minimiser séparément les énergies des états X et I, ce qui conduit à deux jeux d'orbitales moléculaires et donc, à des états non-orthogonaux. En fait, on peut penser également à localiser le croisement de deux courbes de potentiel d'états diabatiques à partir de la position du croisement évité dans la base adiabatique et ainsi obtenir les paramètres intervenant dans la formule de Landau - Zener-Stueckelberg (cf chapitre V).Ainsi, l'interaction au point de croisement, dans la base diabatique, est égale à la moitié de la séparation énergétique au point de croisement évité dans la base adiabatique*. Les états adiabatiques pouvant être obtenus dans un calcul d'interaction de configurations faisant intervenir les orbitales virtuelles de X, on évite ainsi la double minimisation décrite ci-dessus. En fait, les courbes de potentiel des états adiabatiques ne montrent pas la présence nette d'un croisement évité (cf figure 1 - chapitre IX) et l'on ne peut donc retenir cette façon de procéder dans le cas qui nous intéresse ici.

2. La méthode que nous avons retenue revient donc, à grande distance, à minimiser les énergies de Xe et Xe^+.

L'énergie de corrélation (différence entre l'énergie exacte, sans les effets relativistes, et la limite Hartree-Fock) étant plus grande pour Xe que pour Xe^+ (qui contient un électron de moins) on obtient un potentiel d'ionisation de Xe inférieur à la valeur expérimentale. On sera donc amené, par la suite, (cf chapitres V et VI) à "translater" l'état I vers l'état X pour

---

* La détermination précise de la différence des pentes des courbes d'énergie potentielle diabatiques est toutefois plus difficile avec cette méthode.

reproduire la différence d'énergie expérimentale. Cette translation sera effectuée, faute de mieux, en conservant l'interaction calculée. Cette méthode est assez habituelle mais les effets d'une telle opération sont difficiles à estimer.

3. Le calcul du recouvrement entre les états X et I, ainsi que le calcul de l'interaction entre les états orthogonaux X et K, se conduit en développant l'état I sur la base formée de X et des états excités décrits à l'aide des orbitales virtuelles obtenues dans le calcul SCF de l'état X. On obtient ainsi, pour R > 3 Bohrs, le développement très simple :

$$|I\rangle \simeq S|X\rangle + A|I_X\rangle + B|D_X\rangle \qquad (1)$$

où I_X et D_X désignent respectivement les états de configuration ... $11\sigma\ 12\sigma$ et ..... $12\sigma^2$ respectivement monoexcité et diexcité par rapport à X. Le calcul de S, A, B qui sont des termes de recouvrements entre des déterminants de Slater bâtis sur des orbitales moléculaires (O.M.), se ramène au calcul des déterminants formés des recouvrements des O.M./63/. On calcule le recouvrement entre deux O.M. à l'aide d'un sous-programme du programme ALCHEMY. On obtient ainsi, après avoir utilisé le théorème de Brillouin /92/ (il n'y a pas, au premier ordre, d'interaction électronique entre un état SCF à couches complètes et tout état monoexcité par rapport à lui,décrit dans l'approximation des orbitales virtuelles) :

$$\langle K\,^1\Sigma^+ | H_{el} | X\,^1\Sigma^+ \rangle = \frac{B}{\sqrt{1 - S^2}} \langle D_X | H_{el} | X \rangle \qquad (2)$$

Le couplage responsable de l'échange de charge quasi-résonnant, dans les collisions H^+ - Xe, fait donc intervenir l'interaction électronique entre X (.... $11\sigma^2$) et l'état diexcité D (... $12\sigma^2$). Un résultat similaire pour le système collisionnel H^+ + Kr sera obtenu par la suite (cf chapitre VII).

4. L'estimation des termes provenant de l'interaction spin-orbite a été faite de façon à éviter des calculs trop compliqués.

Nous avons utilisé une méthode semi-empirique assez habituelle /93/ où l'opérateur H_{so}, moléculaire, est approché par une somme d'opérateurs mono-électroniques centrés sur Xe et H.

$$H_{so} \simeq H_{so(H)} + H_{so(Xe)} \simeq H_{so(Xe)}$$

où $H_{so(H)}$, et $H_{so(Xe)}$ désignent respectivement les opérateurs spin-orbite des atomes d'hydrogène et de xénon.

En écrivant les O.M. en termes de combinaison linéaire d'orbitales atomiques :

$$12\sigma \simeq a\ 5p_{oXe} + b\ 1s_H$$
$$6\pi \simeq 5p_{1Xe}$$

On ramène le calcul d'intégrales moléculaires telles que :

$\langle 12\sigma \mid H_{so} \mid 6\pi \rangle$ à celui des intégrales atomiques :

$a \langle 5p_{oXe} \mid H_{so(Xe)} \mid 5p_{1Xe} \rangle$ reliées à la séparation énergétique entre $Xe^+ (^2P_{1/2})$ et $Xe^+ (^2P_{3/2})$, expérimentalement connue /94/.

5. Il convient de noter que les états de même symétrie : $X^1\Sigma^+$ et $K^1\Sigma^+$, qui se croisent, ne sont pas pour autant diabatiques, au sens de Smith /36/, puisque l'on obtient, en utilisant la relation (1) :

$$\langle K^1\Sigma^+ \mid \partial/\partial R \mid X^1\Sigma^+ \rangle = \frac{A}{\sqrt{1-S^2}} \langle I_x \mid \partial/\partial R \mid X \rangle$$
$$= \frac{A\sqrt{2}}{\sqrt{1-S^2}} \langle 12\sigma \mid \partial/\partial R \mid 11\sigma \rangle \neq 0$$

On a donc un couplage radial de l'ordre de grandeur de celui que l'on obtient par la méthode des orbitales virtuelles.

6. Les états $\bar{\Phi}^-$ et $\bar{\Phi}^+$ caractérisés par $\Omega = 0$, sont en fait les états 0^+ et 0^- symétriques et antisymétriques dans la réflexion, par rapport à un

plan quelconque passant par l'axe internucléaire. Le découplage de $K^1\Sigma^+$ et Φ^+ se démontre alors en utilisant les propriétés de symétrie de H_{so} /95/. Ce résultat a également été obtenu par Shakeshaft et Macek /31/. Des détails complémentaires sur ce chapitre peuvent être trouvés dans la référence /72/.

Nous pouvons maintenant utiliser la base des trois états $\Omega = 0^+$ pour le calcul des sections efficaces élastique et d'échange de charge quasi-résonnant dans les collisions H^+ - Xe. Ceci est fait dans les deux chapitres suivants, et les sections efficaces différentielles calculées sont comparées aux résultats expérimentaux. Les calculs seront conduits d'une part dans l'approximation Landau - Zener - Stueckelberg que nous avons étendue au cas de deux croisements et, d'autre part en utilisant des méthodes de résolution numérique des équations couplées : celle de Numerov à faible énergie de collision et celle de Gordon à plus grande énergie.

Chapitre V

Theoretical study of the elastic scattering of H^+ by Xe *

C Kubach†, V Sidis‡§ and J Durup†

† Laboratoire des Collisions Ioniques‖, Université de Paris-Sud, 91405 Orsay, France
‡ Centre de Mécanique Ondulatoire Appliquée, 23 rue du Maroc, Paris 75019, France

Received 16 January 1974, in final form 31 December 1974

Abstract. The potential energy curves of $(XeH)^+$ obtained by Kubach and Sidis (1973) are used in the computation of elastic differential cross sections for the scattering of H^+ by Xe. The calculations are carried out either in an extended semiquantal Landau–Zener–Stueckelberg JWKB approximation or by direct numerical integration of quantal three-state close-coupled equations. The oscillations in the elastic cross section are attributed to Stueckelberg-type interferences in contrast with the earlier interpretation of Weise *et al* (1971) of these structures as due to rainbow scattering. Discrepancies at large angles are explained by our neglect of higher molecular states leading to $H^* + Xe^+$ or $H^+ + Xe^*$.

1. Introduction

The elastic differential cross section at low energies in proton–noble gas collisions, which usually exhibits prominent rainbow features, has been shown to be adequately described by considering that the system is scattered by an attractive central potential extracted from *ab initio* molecular calculations (Champion *et al* 1970, Bobbio *et al* 1971, Weise *et al* 1971). It also appeared that experimentalists are becoming able to propose 'experimental' potentials either by using fitting procedures (Champion *et al* 1970, Bobbio *et al* 1971, Weise *et al* 1971) or by directly inverting the scattering data (Doverspike 1973). However Weise *et al* (1971) showed that in the case of $H^+ + Xe$ it was impossible to interpret by the same scattering potential the results obtained at different energies, which revealed the effects of curve-crossings. They gave apparent scattering potentials derived from their experiments at each energy, which of course, do not agree with the usual concepts characterizing the potential governing the motion of the nuclei, at least as far as one is concerned with atom–atom scattering in the perturbed stationary states approach, even if one includes in the potential the adiabatic corrections to the Born–Oppenheimer approximation. On another hand, an energy-dependent potential could only be conceived if either the electronic wavefunction involves translational factors (Ritchie 1970) and even in this case the energy dependence would only show up at high velocities, or if the potential has an imaginary part describing phenomenologically the absorption of particles into other channels. Actually the $(HXe)^+$ system is the first of the $(H–rare\ gas)^+$ series, except for $(HKr)^+$ for which a 'quasi-resonance' occurs, which is expected to involve a crossing or pseudo-crossing (according to whether one adopts a diabatic or an adiabatic point of view) between the two lowest $^1\Sigma^+$ molecular potential energy curves dissociating into either $H^+ + Xe(^1S)$ or $H(^2S) + Xe^+(^2P)$ (Weise *et al* 1971, Abignoli

§ Present address: Laboratoire des Collisions Atomiques, Université de Paris-Sud, 91405 Orsay, France.
‖ Part of the Laboratoire de Physico-Chimie des Rayonnements, associated to the CNRS.

* J. Phys. B: Atom. Molec. Phys., Vol. 8, No. 7, 1975. Printed in Great Britain. © 1975

et al 1972, Kubach and Sidis 1973). In such a case, even at the lowest collision energies, any theoretical treatment of the elastic scattering should take into account at least two states. On the other hand, any known, as yet, procedure for inverting the scattering data for $(HXe)^+$ would fail. In fact, in the $(HXe)^+$ system the non-negligible spin–orbit coupling effects should aso be considered and necessitate not only a two-state but a three-state approach (Kubach and Sidis 1973) in the investigation of the elastic scattering at low energies and moderate scattering angles.

We report here the results of calculations, on the elastic processes, which involve:

(i) the single state $x\,^1\Sigma^+$,

(ii) the three potential energy curves corresponding to the coupled states $x\,^1\Sigma^+$, ϕ_1 and ϕ_2 (with $\Omega = \Lambda + \Sigma = 0$) of Kubach and Sidis (1973) in two different ways, namely:

(*a*) semiquantal approximation involving Landau–Zener–Stueckelberg probabilities, at two crossings points, and JWKB phase shifts;

(*b*) direct numerical integration of the coupled second-order differential equations.

The effect of higher excited molecular states will finally be discussed qualitatively in connection with the scattering at large values of the reduced angle $\tau = E\theta$.

2. Scattering by the single potential $x\,^1\Sigma^+$

2.1. Analytical fit to the potential

As in the work of Sidis (1972) the $x\,^1\Sigma^+$ potential energy curve of $(XeH)^+$ (Kubach and Sidis 1973) has been fitted using a modified Morse potential:

$$V(R) = U(X^2 - 2X) \tag{1}$$

where

$$X(R) = (R_e/R)^a \exp[b(R_e - R)] \tag{2}$$

with $U = 0{\cdot}2129$ hartree being the absolute value of the well depth and $R_e = 3$ bohrs the internuclear equilibrium distance. The other parameters were determined as:

$$\left.\begin{aligned} a &= 0{\cdot}44 \\ b &= 0{\cdot}605\ \text{bohr}^{-1} \end{aligned}\right\} R \leqslant R_e$$

$$\left.\begin{aligned} a &= 1 \\ b &= 0{\cdot}51\ \text{bohr}^{-1} \end{aligned}\right\} R \geqslant R_e.$$

2.2. Results

The computational procedure has already been described by Sidis (1972). The elastic differential cross section involving the single $x\,^1\Sigma^+$ potential at 18·2 eV is shown in figure 1; it exhibits the double oscillatory behaviour characterizing rainbow scattering due to an attractive and repulsive potential (see Champion *et al* 1970 for instance). This result appears to be in disagreement with the experimental cross section (figure 4, curve A). In particular, the primary rainbow is located around 21° in the computed cross section while it is found around 30° in the experimental data. We have also found similar discrepancies at other energies ($\leqslant 60$ eV).

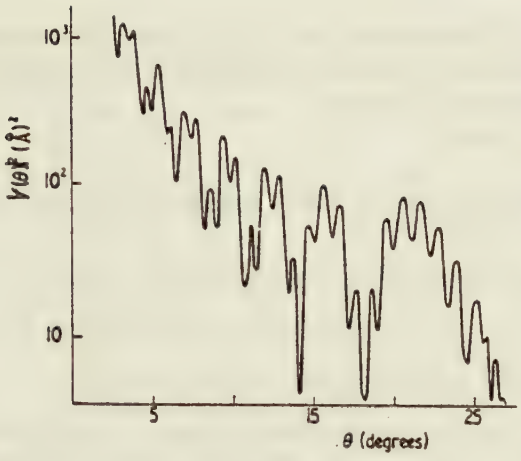


Figure 1. Semiquantal elastic differential cross section at 18·2 eV computed using the potential energy curve of the $x\,^1\Sigma^+$ state.

3. Three-state approximation

The three states involved here are those with $\Omega = 0$ corresponding to the potential curves X, (1) and (2) in figures 1 and 2 of Kubach and Sidis (1973). The curves (1) and (2) have been shifted upwards by 0·026 hartree (0·71 eV) to reproduce the experimental energy separation at infinity between $Xe(^1S) + H^+$ and $Xe^+(^2P_{1/2}) + H(^2S)$ (Moore 1958).

3.1. Extension of the Landau–Zener–Stueckelberg approximation to the case of three states

Since the original studies of Landau (1932), Zener (1932), and Stueckelberg (1932) a large number of authors have been concerned with the investigation of the range of validity of the LZS method as well as with various improvements to which it could be submitted. The most recent such work can be found in the thorough analysis of the model given in a series of papers by Delos *et al* (1971, 1972) and Thorson *et al* (1971). Some literature has also appeared on the 'multistate-crossing' problem (Green and Thorson 1966, Nikitin 1968, Bobashev 1971, Ostrovsky 1973 and Afrosimov 1973). The point of view which is adopted in the present work consists first in assuming that at each crossing R_c^l, between two states N and M, the probability for the system to remain on the diabatic state in a single passage through R_c^l is given by the Landau–Zener model as

$$P_{l,l}^{NM} = \exp\left(\frac{-2\pi H_{NM}^2}{v_R^l \Delta F_{NM}}\right) \tag{3}$$

where v_R^l is the radial velocity for the lth partial wave, H_{NM} the coupling between the two diabatic states N and M and ΔF_{NM} the absolute value of the difference in slopes between the two corresponding diabatic potentials. All the quantities are expressed in atomic units at the crossing point. Moreover, all probabilities linking a pair of states are considered to be independent of each other (Nikitin 1968). On another hand one may write down an element of the scattering S matrix as a sum of probability amplitudes each of which is considered here 'semiclassically' as the square root of a semiclassical probability (for instance, products of the above P_i or $1 - P_i$) weighted by a phase factor

which according to Miller (1970) appears to be a JWKB phase shift developed along the relevant path. The trivial case is that of a single potential with no crossing at all for which P_i equals 1, giving for the scattering S matrix

$$S_{11}^{(0)l} = \exp(2i\delta_1^{l(\mathrm{JWKB})}) \tag{4}$$

which is the expression used in § 2. In the case of a single curve-crossing between two states the result is (writing $\delta_i^l = \delta_i^{l(\mathrm{JWKB})}$)

$$\begin{aligned} S_{11}^{(1)l} &= P_{1l}^{12}\exp(2i(\delta_1^l+\delta_2^l))+(1-P_{1l}^{12})\exp(2i(\delta_1^l+\delta_3^l)) \\ S_{12}^{(1)l} &= (P_{1l}^{12})^{1/2}(1-P_{1l}^{12})^{1/2}[\exp(2i\delta_3^l)-\exp(2i\delta_2^l)]\exp(i(\delta_1^l+\delta_4^l)) = S_{21}^{(1)l} \\ S_{22}^{(1)l} &= P_{1l}^{12}\exp(2i(\delta_4^l+\delta_3^l))+(1-P_{1l}^{12})\exp(2i(\delta_4^l+\delta_2^l)) \end{aligned} \tag{5}$$

labelling the different parts of the available paths as in figure 2. The model neglects any eventual additional phase factor such as those described by Delos *et al* (1972), Bobashev (1971) and others. This assumption has been made for simplicity to avoid tedious

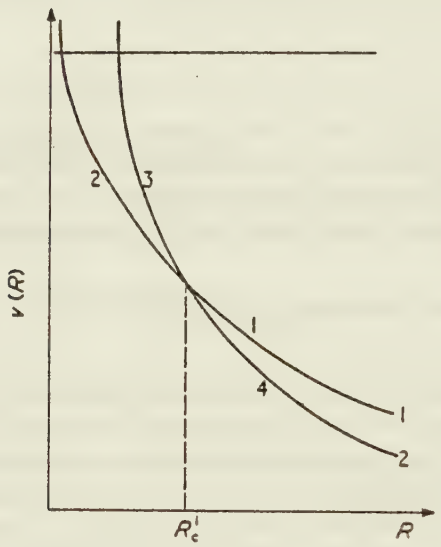


Figure 2. Single crossing: paths corresponding to the phase shifts of equations (5).

derivations (Delos *et al* 1972) in the more complicated case of several crossings. It may be noticed however that the matrix element S_{11}^{1l} is the same as that obtained by Delos and Thorson (1972) in their 'adiabatic perturbation approximation'. On the other hand, the expression (5) has also been used either explicitly or not in the previous works of Marchi (1969), Olson and Smith (1971), Delvigne and Los (1973) and Evans and Lane (1973). In the case of the two-crossing-points problem of interest to us here (figure 3) one has according to the above procedure:

$$\begin{aligned} S_{XX}^{(2)l} = \exp(2i\delta_1^l)[&P_{1l}^{X1}P_{2l}^{X2}\exp(2i(\delta_2^l+\delta_3^l))+P_{1l}^{X1}(1-P_{2l}^{X2})\exp(2i(\delta_2^l+\delta^l{}_7)) \\ &+(1-P_{1l}^{X1})\exp(2i\delta_5^l)]. \end{aligned} \tag{6}$$

The other matrix elements of S can be obtained in the same way by taking care in choosing the correct relative sign of the various terms to ensure the unitarity of the S matrix (as was done in (5) for S_{12}^{1l}).

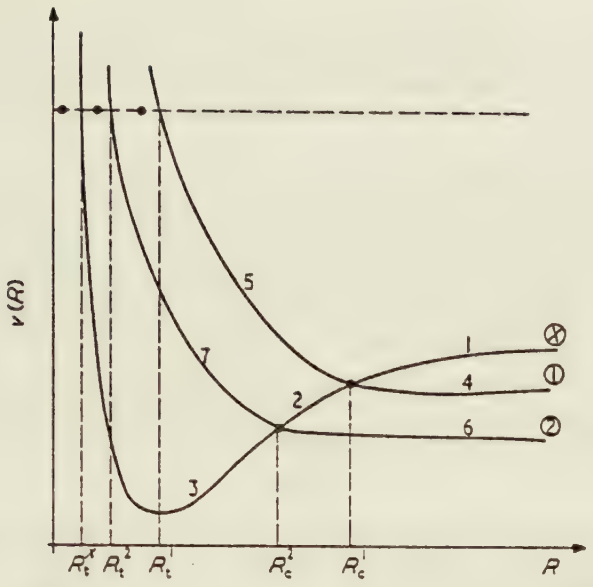


Figure 3. Two crossings: paths corresponding to the phase shifts of equation (6).

The elastic scattering amplitude is then

$$f_{xx}(\theta) = \frac{1}{2ik_0} \sum_{l=0}^{\infty} (2l+1)(S_{xx}^{(2)l} - 1)P_l(\cos\theta). \tag{7}$$

3.1.1. Details of computation. The JWKB phase shifts were computed in the same way as in § 2.2. The P_{ll}^{NM} probabilities involve at $R_c^1 = 10{\cdot}0$ bohr and $R_c^2 = 6{\cdot}25$ bohr the coupling matrix elements $H_{x1} = -0{\cdot}0044$ hartree and $H_{x2} = -0{\cdot}032$ hartree respectively. These probabilities were set equal to 1 for all distances of closest approach R_t^i larger than their corresponding R_c^i. One could still improve upon this feature of the LZ model by allowing for 'tunnelling' (Nikitin 1968). The scattering amplitude was then computed as the sum (7) up to an l_{max} related to the effective range of the potentials. This procedure called 'semiquantal' unlike that involving the 'semiclassical' stationary phase approximation allows a simple treatment of the range of l values where the deflection function passes through a minimum (Olson and Smith 1971, Kotova and Ovchinnikova 1971) especially in the case of multicrossings and rainbow effects, where several points of stationary phase may lie close to each other.

3.1.2. Results. The semiquantal cross sections at the collision energies $E = 18{\cdot}2$ eV and $E = 30$ eV obtained using the above technique are displayed in figures 4 and 5 respectively (curve B) together with the experimental results (curve A) for comparison. Good agreement is seen for scattering angles less than θ_d such that:

$$\tau_d = \theta_d E \simeq 600 \text{ eV deg.}$$

Above this reduced angle, the Stueckelberg oscillations are persisting while a fall-off is observed in the experimental data. This discrepancy is found at all other energies investigated. This means in our sense that some additional processes are occurring at a constant distance of closest approach. This effect will be discussed in § 4.

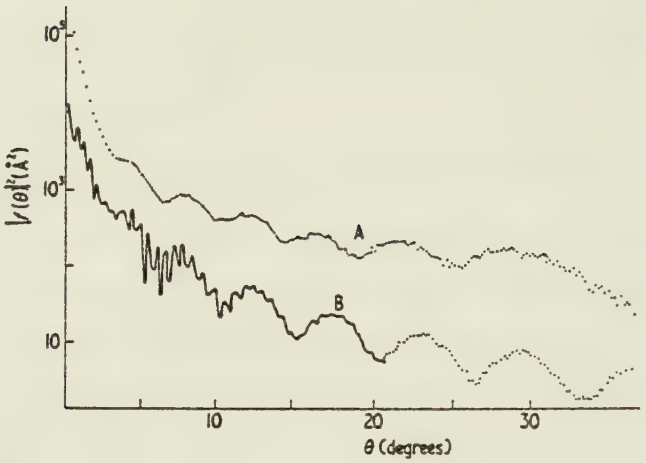


Figure 4. Semiquantal differential cross section at 18·2 eV in the LZS, JWKB approximation (curve B) (the RHS of curve B exhibits the rough results; on the LHS the points have been joined by a full line for the sake of clarity). The experimental result, in arbitrary units (curve A), is shown for comparison.

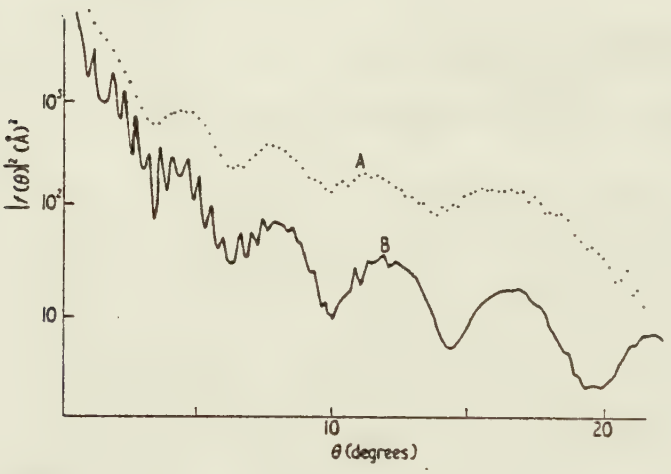


Figure 5. Semiquantal differential cross section at 30·0 eV in the LZS, JWKB approximation (curve B). The experimental result, in arbitrary units (curve A), is shown for comparison.

3.2. Numerical integration of the quantal three-state close-coupled equations

The three-state close-coupled equations

$$\left(\frac{d^2}{dR^2}+2\mu(E-V_{ii}(R))-\frac{l(l+1)}{R^2}\right)g_l^i(R)=\sum_{j\neq i}2\mu H_{ij}(R)g_l^j(R), \tag{8}$$

where the labels 1, 2, 3 correspond to the states X, ϕ_1 and ϕ_2 respectively, were solved numerically for all values of l up to $l_{max} = kA$ (with A the effective range of the potential = 20 bohr) by using the Numerov algorithm as described by Lane and Geltman (1967). The elements S_{ij}^l of the scattering matrix could thus be extracted from the asymptotic ($R \to \infty$) behaviour of the wavefunction. The criteria of Evans *et al* (1971) were used to

check our computer program (symmetry of the reactance R matrix, unitary S matrix when all $V_{ii} = 0$ and $H_{ij} = 0$). The stability of the solutions against reasonable variations of the integration parameters (step size, starting distance of integration inside the classically forbidden region) was also verified.

3.2.1. Results and discussion. The elastic quantal differential cross section at 18·2 eV collision energy involving the $H_{ij}(R)$ matrix elements of figure 6 is shown in figure 7 (curve A). The LZS semiquantal result of § 3.1.2 is displayed on the same plot (curve B). These two curves show, in contrast to that of figure 1, the persistence of oscillations at scattering angles larger than 25°. This feature is illustrative of the effects of inelastic transitions on the elastic cross section. At angles smaller than 25°, rainbow scattering is expected to complicate the effect of the above transitions. It is worth mentioning at this point that the LZS probability P_{21}^{X2} is, at 18·2 eV, very low ($< 10^{-2}$) so that the 1–2–7 and 4–5 potentials of figure 3 are those actually involved in the scattering. The

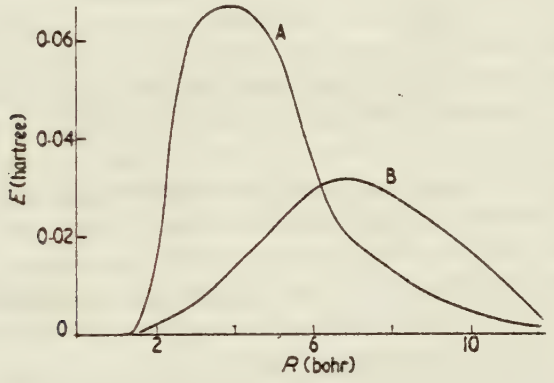


Figure 6. Absolute values of the interactions between states $X\,^1\Sigma^+$ and ϕ_1 (curve A) and $X\,^1\Sigma^+$ and ϕ_2 (curve B). These interactions are matrix elements of the $H_{el} + H_{\infty}$ operator.

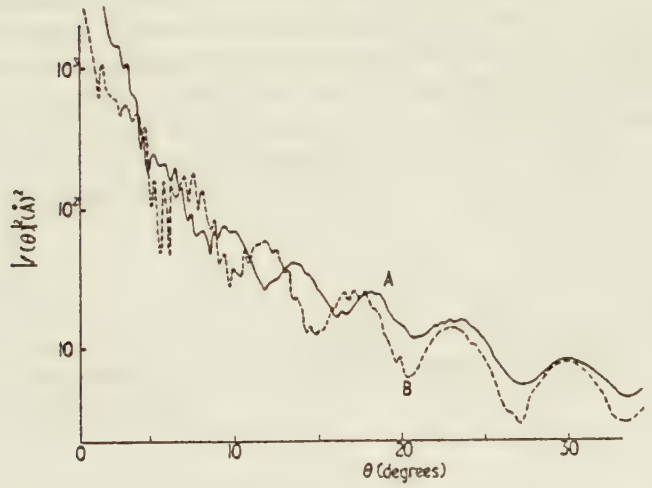


Figure 7. Elastic differential cross section at 18·2 eV obtained by numerical integration of the three-state coupled equations (curve A). The LZS, JWKB result is shown for comparison (curve B).

smallness of the $|S_{X2}^{(2)l}|^2$ quantal scattering matrix elements (Kubach *et al* to be published) also supports this conclusion. As a consequence, the pure elastic scattering by the actual potential 1–2–7 of figure 3 throws the rainbows at a smaller angle than that of figure 1 (5° instead of 21°). Also, the presence of only one dominant frequency at angles larger than 10° in the curves of figure 7 reflects the fact that the system is mainly scattered by the two potentials 1–2–7 and 4–5 of figure 3 which give rise to Stueckelberg oscillations.

Comparison of the two cross sections of figure 7 shows that they are in fair agreement as regards the general shape but the oscillations are of different amplitude and, in the range 6° to 18°, not in phase. These discrepancies are attributed to the inherent defects of the LZS model. Indeed:

(i) The quantal result takes into account transitions occurring in a wider range of internuclear distances than assumed in the LZS approximation; such transitions which are not strongly localized around the crossing radii tend to reduce the amplitude of the oscillations.

(ii) The LZS semiquantal scattering element used here for elastic scattering (equation 6) neglects the additional phase shifts discussed by Thorson *et al* (1971), Child (1971) and Nikitin and Reznikov (1972). The addition of phase shifts y_1^l and y_2^l at each crossing point might reduce the shift between the quantal and semiquantal cross sections of figure 7. However, we have found (Kubach *et al* to be published) that the LZS semiquantal cross section at 18·2 eV is not significantly modified when the phase shifts $y_1^l = y_2^l = \frac{1}{4}\pi$ (Nikitin and Reznikov 1972) are taken into account.

(iii) The LZS transition probability takes no account of 'underbarrier transitions'. These underbarrier transitions from the $X\,^1\Sigma^+$ state to the ϕ_1 state are found to be important, as shown in figure 8. Effects of such transitions can also contribute to the discrepancies between the A and B cross sections of figure 7.

Comparison of the quantal result with experiment (figure 9) shows that some defects are still remaining. These are due to the high sensitivity of the quantal cross sections to inaccuracies in the potential energy curves and coupling terms which for a system as complicated as $(Xe–H)^+$ (involving 54 electrons) can only be calculated with moderate precision. Indeed, the replacement of the $\langle\phi_2|H|X\,^1\Sigma^+\rangle$ curve of figure 6 by a curve of the same shape, but with a width at half-maximum twice as large, leads to a drastic smoothing of the oscillations (Kubach 1974).

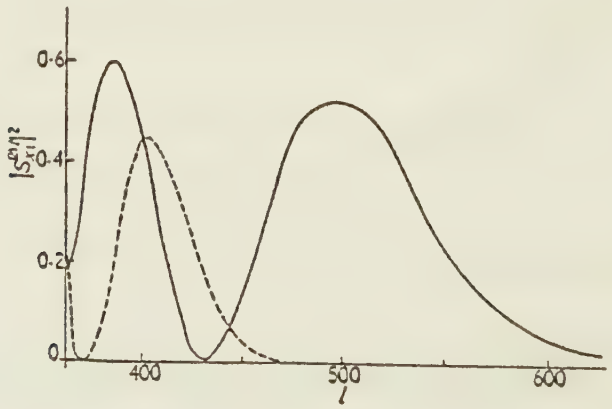


Figure 8. Transition probability $|S_{X1}^{(2)l}|^2$ for large l at 18·2 eV. – – – – LZS semiquantal result, ——— quantal result. For $l = 495$ the turning points of X and (1) potentials are R_c^1 (see figure 3).

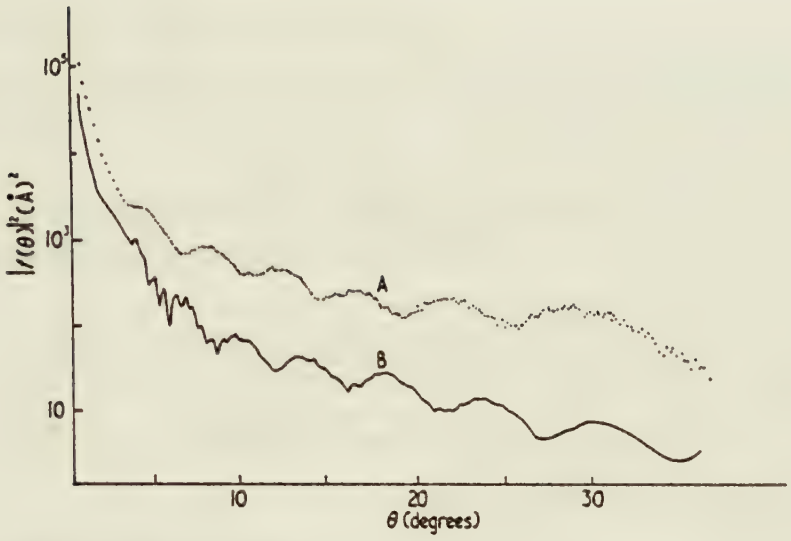


Figure 9. Comparison between quantal elastic differential cross section (curve B) in Å^2 and experimental result (curve A) in arbitrary units at 18·2 eV.

The excellent agreement of the LZS cross section with the experimental one is accidental since the model is designed to approximate the quantal result.

4. Effects of higher molecular states

Figure 2 of Kubach and Sidis (1973) displays the crossing of some potential curves of excited states, dissociating into $H(n = 2) + Xe^+$ and $H^+ + Xe^*$, with the curves (1) and (2). These sample the great number of crossings at internuclear distances smaller than $4 \pm 0{\cdot}25$ bohr which should be responsible for the absorption of the system into excitation channels at the corresponding reduced angle $\tau \simeq 600$ eV deg. This is confirmed by the experimental results of Abignoli *et al* (1972) which exhibit a strong fall-off of the elastic cross section and an important enhancement of inelastic processes at larger τ. This effect will most probably damp out the Stueckelberg oscillations with simultaneous attenuation of the elastic cross section, thus explaining the apparent discrepancy of figures 4 and 5, and helping us understand why the oscillations in the elastic cross section were attributed to rainbow scattering by Weise *et al* (1971).

Acknowledgments

We wish to thank Professor A Henglein and Dr H P Weise who communicated to us some unpublished data, and Dr H Fremerey who gave us useful subroutines for the calculation of Bessel functions.

References

Abignoli M, Baudon J, Barat M, Fayeton J and Houver J C 1972 *J. Phys.* B: *Atom. Molec. Phys.* 5 1533–53

Afrosimov V V 1973 *Proc. 8th Int. Conf. on Physics of Electronic and Atomic Collisions, Belgrade* (Beograd: Institute of Physics) p 210

Bobashev S V 1972 *Proc. 7th Int. Conf. on Physics of Electronic and Atomic Collisions, Amsterdam* Progress report (Amsterdam: North-Holland) p 38
Bobbio S M, Rich W G, Doverspike L D and Champion R L 1971 *Phys. Rev.* A **4** 957–64
Champion R L, Doverspike L D, Rich W G and Bobbio S M 1970 *Phys. Rev.* A **2** 2327–34
Child M S 1971 *Molec. Phys.* **20** 171–84
Delos J B and Thorson W 1972 *Phys. Rev.* A **6** 709–19, 728–45
Delos J B, Thorson W and Knudson S 1972 *Phys. Rev.* A **6** 720–7
Delvigne G A L and Los J 1973 *Physica* **67** 166–95
Doverspike L D 1973 *Proc. 8th Int. Conf. on Physics of Electronic and Atomic Collisions, Belgrade* (Beograd: Institute of Physics)
Evans S A, Cohen T S and Lane N F 1971 *Phys. Rev.* A **4** 2235–48
Evans S A and Lane N F 1973 *Phys. Rev.* A **8** 1385–96
Green T A and Thorson R E 1966 *Phys. Rev.* A **152** 9–20
Kubach C 1974 *Thèse de Doctorat de Spécialité* Paris
Kubach C and Sidis V 1973 *J. Phys.* B: *Atom. Molec. Phys.* **6** L289–93
Kotova L P and Ovchinnikova M Y 1971 *Sov. Phys.–JETP* **33** 1092–8
Landau L 1932 *Phys. Z. Sowjun.* **2** 46–51
Lane N and Geltman S 1967 *Phys. Rev.* A **160** 53–67
Marchi R P 1969 *Phys. Rev.* A **183** L85–92
Miller W H 1970 *J. Chem. Phys.* **52** 3563–72
Moore C E *Atomic Energy Levels, NBS Circular No* 467 vol 3 (Washington, DC: US Govt Printing Office)
Nikitin E E 1968 *Chemische Elementarprozesse* ed H Hartmann (Berlin: Springer-Verlag) pp 43–77
Nikitin E E and Reznikov A I 1972 *Phys. Rev.* A **6** 522–3
Olson R E and Smith F T 1971 *Phys. Rev.* A **3** 1607–17
Ostrovsky V N 1973 *Proc. 8th Int. Conf. on Physics of Electronic and Atomic Collisions, Belgrade* (Beograd: Institute of Physics) p 133
Ritchie B 1970 *Phys. Rev.* A **2** 759–62
Sidis V 1972 *J. Phys.* B: *Atom. Molec. Phys.* **5** 1517–28
Stueckelberg E C G 1932 *Helv. Phys. Acta.* **5** 369–422
Thorson W, Delos J B and Boorstein S A 1971 *Phys. Rev.* A **4** 1052–66
Weise H P, Mittmann H P, Ding A and Henglein A 1971 *Z. Naturf.* **26a** 1112–28
Zener C 1932 *Proc. R. Soc.* A **137** 696–702

Chapitre VI

Charge-exchange processes in collisions between protons and rare gases I. $H^+ + Xe$ *

C Kubach†, C Benoît†, V Sidis‡§, J Pommier‡ and M Barat‡

†Laboratoire des Collisions Ioniques‖, Bâtiment 420, Université Paris-Sud, 91405 Orsay, France

‡Laboratoire des Collisions Atomiques‖, Bâtiment 220, Université Paris-Sud, 91405 Orsay, France

Received 6 January 1976, in final form 26 March 1976

Abstract. Charge-exchange processes in the H^+Xe system have been investigated in the angular and energy ranges $0{\cdot}2 < \theta < 3$ deg, $60 \leqslant E \leqslant 600$ eV. The time-of-flight analysis of the scattered neutrals allows the identification of the lowest electron-transfer channels $H(1s) + Xe^+(5p^5\ ^2P_{1/2,3/2})$. In addition charge exchange into higher excited states is also observed. The relative differential cross sections exhibit an oscillatory behaviour as a function of the product $E\theta$. The interpretation is carried out in the quasi-molecular framework. Theoretical investigation of the $H(1s) + Xe^+(^2P_{3/2,1/2})$ channels involves the three lowest $|\Omega = 0^+\rangle$ states of the $(XeH)^+$ molecule. Differential cross sections are calculated using the Landau–Zener–Stueckelberg approximation and the solutions of the three quantal close-coupled equations. The structures appearing in the differential cross sections are attributed to inelastic rainbow effects and to Stueckelberg-type interferences. Agreement between theory and experiment is encouraging.

1. Introduction

Until 1967, most of the experimental (Stedeford and Hasted 1955, Koopman 1967) and theoretical (Rapp and Francis 1962) research on $H^+ + Xe$ collisions was devoted to the study of total charge-transfer cross sections. Although at that time, Fleischmann and Young (1967) referred to differential measurements of charge-exchange cross sections, the resulting data were not reported. Later, Weise *et al* (1971) investigated the elastic scattering of protons by Xe atoms at low energy ($E < 60$ eV) and stressed the difficulty of extracting from their data a unique scattering potential. These experiments were then complemented at higher energies ($0{\cdot}5 \leqslant E \leqslant 2$ keV) by the differential cross section measurements of Abignoli *et al* (1972) on elastic, direct-excitation and charge-transfer processes. However, that experiment could not resolve the final states of the atomic species produced by charge transfer. To our knowledge, the first study of electron capture into the selected $H + Xe^+(^2P_{1/2 \text{ or } 3/2})$ levels was carried out theoretically by Shakeshaft and Macek (1972). However, since the primary interest of these authors was to demonstrate that $H^+ + Xe$ collisions could produce spin-polarized H atoms most of their effort and the results they published were mainly

§ CMOA, 23 rue du Maroc, 75019 Paris, France.

‖ Associated with the CNRS.

* J. Phys. B: Atom. Molec. Phys., Vol. 9, No. 12, 1976. Printed in Great Britain. © 1976

devoted to electron capture into $H + Xe^+(^2P_{1/2})$ at low energy ($E \sim 15$ eV). The experimental determination of doubly differential charge-transfer cross section for well resolved $H + Xe^+(^2P_{1/2}$ or $^2P_{3/2})$ levels was made recently, using a time-of-flight (TOF) technique (Benoît *et al* 1974). The use of D^+ ions in that experiment enabled the measurement of cross sections corresponding to $H^+ + Xe$ collisions at energies $50 \leqslant E \leqslant 350$ eV. The present experiment (involving H^+ ions) extends this range to higher proton energies where charge-exchange excitation processes are sufficiently important to be measured. In §2 unpublished data from the earlier work of Benoît *et al* (1974) and new results are presented.

The previous total cross section measurements of Koopman (1967) demonstrated that charge exchange in the $H^+ + Xe$ system is an important process at energies as low as 50 eV. According to the Massey criterion (Massey 1949) one indeed expects large total cross sections for electron capture into $H + Xe^+(^2P_{1/2})$ since this level lies only 0·17 eV below $H^+ + Xe(^1S_0)$. Although the Massey criterion predicts that the *total cross section* for charge exchange into $H + Xe^+(^2P_{3/2})$ will not become appreciable until proton energies of about 1·8 keV (Shakeshaft and Macek 1972) the results of Benoît *et al* (1974) show that the *differential cross sections* for this process may become of the same order of magnitude as that of $H + Xe^+(^2P_{1/2})$ for certain angles and at a few hundred eV collision energies. This effect, as well as the perturbations of the elastic cross section (Weise *et al* 1971, Kubach *et al* 1975) together with the Xe direct excitation (Abignoli *et al* 1972) and charge transfer into higher states, should be related to molecular interactions and in particular to curve-crossing mechanisms (Abignoli *et al* 1972, Kubach *et al* 1975). The Landau–Zener–Stueckelberg model provides the simplest approximation for treating curve-crossing problems. Although it has repeatedly been demonstrated that the conditions of validity of this model are seldom if ever met, it has often been applied, rather successfully, in a wider range than that predicted from a thorough analysis of the model. As in a previous investigation on the perturbed elastic scattering of H^+ by Xe (Kubach *et al* 1975), it is interesting to know the results of an extended 'three-state LZS model' calculation in the case of the near-resonant charge-transfer problem of the $H^+ + Xe$ system. In §3 a brief description of the molecular three-state approximation is given and in §4.1 the LZS–JWKB formulation of the two-curve-crossing problem is outlined. In an attempt to determine whether the LZS treatment, the calculated molecular properties (Kubach and Sidis 1973) or the three-state approximation is the source of eventual failures, we have also carried out three-state quantal close-coupling calculations. The results are compared with those of the LZS treatment and with experiment in §§4 and 5. Finally, the features seen in the experimental and in the theoretical cross sections are interpreted (§5) by analysing the deflection functions associated with the classical motion of the system along the different branches of the three molecular potentials.

2. Experiments

The doubly differential measurements of charge-transfer processes were carried out, in the $60 < E < 600$ eV proton energy range and in the $0{\cdot}2 < \theta < 3$ degrees angular range, using a time-of-flight analysis of the energy losses ΔE undergone by the neutral H atoms scattered from the $H^+ + Xe$ collision. Since a detailed description of the

spectrometer has been given previously by Brenot *et al* (1975a,b) only a brief survey of the experimental set-up will be given here.

The ions produced in low-pressure, low-voltage hot-cathode positive-ion glow discharge are focused and collimated by a 0·2 mm wide slit. The ions pass through a parallel-plate capacitor which is used to 'chop' the beam. The chopping voltage is a square-wave pulse (± 10 V) whose frequency, adjustable between 0·1 MHz to 1 MHz, is stabilized by a 20 MHz quartz oscillator. The beam next enters the scattering cell through a second 0·2 mm slit. The scattered ions are swept out by an electric field at the exit of the collision chamber. The time spent by the scattered neutrals to reach the detector is measured by a standard technique involving a time-to-amplitude converter and a pulse-height analyser. The energy calibration, related to the ΔE energy-loss scale, is obtained by using a delay line. Since a TOF apparatus is a velocity selector, by suitably choosing the chopping frequency one can easily get rid of any perturbing contribution coming from the H_2^+ and H_3^+ ions also produced in the source.

The energy spread in the scattered beam has several origins: the ion-source spread, the thermal motion of the target and effects resulting from the finite angular resolution as in conventional spectrometers. Further, the time jitter involved in the electronics itself gives rise to an energy broadening. Nevertheless at beam energies below 0·5 keV the energy resolution is mainly governed by the ion-source energy spread and is typically 0·4 eV. As energy increases above 0·5 keV the energy resolution gradually worsens (e.g. at $E = 800$ eV the energy resolution is 1·5 eV).

The overall angular resolution, determined by the entrance slit of the collision chamber and by the window placed in front of the detector, is approximately 0·2 deg. The zero angle is determined by the measurements of the count rate $N(\theta)$ on both sides of the incident beam axis. The uncertainty in this determination of the angular origin is about 0·05 deg. The Lyman-α light emitted by the ion source produces a saturation of the detector near zero degrees. This effect imposes a lower limit of 0·2 deg on the angular range. In addition at small angles the apparatus function is not well defined. Consequently the data taken at angles $\theta \leqslant 0{\cdot}4$ deg are estimated to be less accurate than those obtained at larger angles. The error in the reproducibility of the data amounts to 10%.

2.1. Spectra

Typical energy-loss spectra are shown in figure 1. The well resolved peaks A and B proceed from the reactions:

$$\text{A}\quad H^+ + Xe \rightarrow H(n=1) + Xe^+(5p^5\ {}^2P_{1/2}) \qquad \Delta E = -0{\cdot}17\text{ eV}$$

$$\text{B}\quad H^+ + Xe \rightarrow H(n=1) + Xe^+(5p^5\ {}^2P_{3/2}) \qquad \Delta E = -1{\cdot}5\text{ eV}.$$

At high energy and large angle ($\tau \gtrsim 300$ eV deg) the following excitation processes of H and Xe^+ are observed:

$$\text{C}\quad H^+ + Xe \rightarrow H(n=2) + Xe^+(5p^5\ {}^2P_{3/2}) \qquad \Delta E = +8{\cdot}7\text{ eV}$$

$$\text{D}\begin{cases} H^+ + Xe \rightarrow H(n=1) + Xe^+(5s5p^6\ {}^2S_{1/2}) & \Delta E = +9{\cdot}83\text{ eV} \\ H^+ + Xe \rightarrow H(n=2) + Xe^+(5p^5\ {}^2P_{1/2}) & \Delta E = +10{\cdot}03\text{ eV}. \end{cases}$$

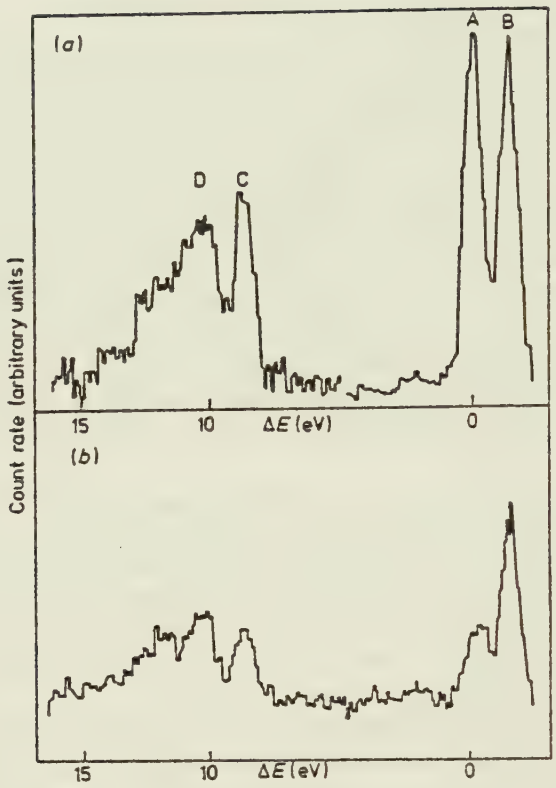


Figure 1. TOF energy-loss spectra of H atoms scattered from the $H^+ + Xe$ collision at: (*a*) $E = 500$ eV, $\theta = 0{\cdot}75$ deg; (*b*) $E = 500$ eV, $\theta = 1{\cdot}35$ deg. Processes A, B, C and D are defined in the text.

2.2. Cross sections

The results are presented as relative reduced cross sections $\rho = \theta\sigma(\theta)\sin\theta$ as a function of the reduced angle $\tau = E\theta$, where E and $\sigma(\theta)$ are respectively the beam energy and the usual differential cross section. In the angular range investigated ρ is proportional to the count rate multiplied by θ^2 (Filippenko 1960, Sauers and Thomas 1974). The reduced cross sections ρ_A and ρ_B corresponding to processes A and B are presented in figures 2 and 3 (see also figures 6, 7 and 9) at various beam energies. Below 100 eV only process A is observed. As energy increases ($E \geqslant 200$ eV) ρ_B grows rapidly and competes with ρ_A (figure 3, see also figures 7 and 9). The rapid variation with τ of the relative magnitude of ρ_A and ρ_B was already shown in a preliminary report (Benoît *et al* 1974). At beam energies $E \geqslant 400$ eV and for $\tau > 500$ eV deg, ρ_A and ρ_B exhibit a fall-off tentatively attributed to the opening of higher excited channels. It is noticeable that ρ_A falls off more rapidly than ρ_B. This seems to indicate that the transition to higher excited channels occurs at smaller impact parameters for the B process than for the A process. The difference between the τ value for the fall-off in the ρ_A cross section and that for the threshold of the ρ_C and ρ_D cross sections will be discussed in §5.

The computation of absolute values for the differential cross sections by referring to previous total charge-transfer cross sections (Koopman 1967) was not attempted since the largest contributions to total cross sections come from small scattering angles for which the present data for ρ_A and ρ_B are either incomplete or insufficiently

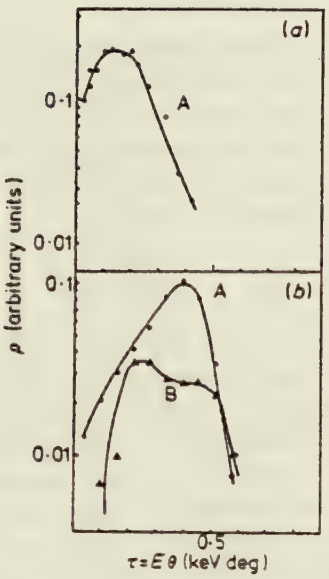


Figure 2. Experimental reduced cross sections for the A and B processes produced in the $D^+ + Xe$ collision at (*a*) $E = 120$ eV and (*b*) 300 eV. These data correspond to $H^+ + Xe$ collisions at $E = 60$ eV and 150 eV.

accurate (see above). The charge-transfer excitation data (ρ_C and ρ_D) could have also been normalized by referring to the total cross section measurements of Jaecks *et al* (1965). Unfortunately these authors have only reported data for energies above 1 keV which are outside our energy range. A valid comparison with the data of

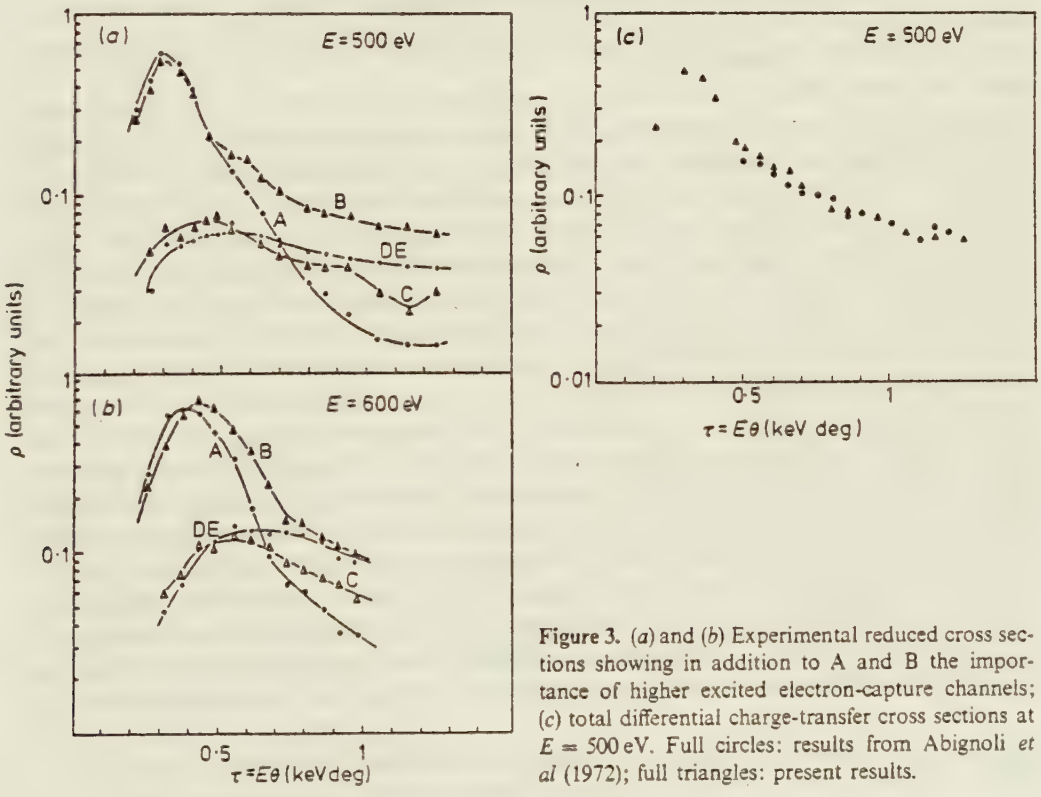


Figure 3. (*a*) and (*b*) Experimental reduced cross sections showing in addition to A and B the importance of higher excited electron-capture channels; (*c*) total differential charge-transfer cross sections at $E = 500$ eV. Full circles: results from Abignoli *et al* (1972); full triangles: present results.

Abignoli *et al* (1972) would have been obtained by bringing into coincidence the total differential charge-transfer cross section of Abignoli *et al* (1972) with the sum of the ρ_A and ρ_B cross sections at small τ values where charge-transfer excitation processes are negligible. The consistency of the two sets of data could have been checked by the quality of the agreement at larger τ values. Nevertheless figure 3(*a*) shows that at least the shapes of the old and new data agree.

3. The basic molecular approach

The qualitative interpretation of the experimental data can start from molecular diabatic correlation diagrams (Barat and Lichten 1972, Abignoli *et al* 1972). The important feature of the molecular orbital (MO) correlation diagram (see figures 25 and 26 of Abignoli *et al* 1972) is the necessary promotion of the $1s_H$ orbital to $4f\sigma$. This orbital then successively crosses the MO issuing from $5p_{Xe}$ and higher lying MO correlated with either H or Xe orbitals. The outermost crossings are thus responsible for the production of processes A and B whereas the channels C, D, ... are fed at the innermost crossings. Therefore processes A and B are expected to show up at smaller τ values than those characterizing the onset of processes C and D; this effect is indeed seen in the experiments. The above molecular scheme is further confirmed by the potential energy curves (figure 4) calculated by Kubach and Sidis (1973). By taking account of the spin–orbit splitting between the $H + Xe^+(^2P_{1/2})$ and the $H + Xe^+(^2P_{3/2})$ levels, it is readily seen (figure 4) that the molecular energy curves associated with channel A will be the first to cross the excited curves. This explains why channel A suffers from absorption effects at smaller τ values than channel B (see figure 3). Since the inner transition region is crowded by a large number of excited states, correlated with $H^* + Xe^+$, $H^+ + Xe^*$, $H + Xe^{+*}$ levels, it can hardly be submitted to a more detailed quantitative analysis. On the other hand, the well isolated A and B channels seem to lend themselves better to a further theoretical investigation. However, it should be kept in mind that the total number of molecular states, coming out of the separated atom states: $H^+ + Xe(^1S_0)$ (labelled X throughout) and $H(^2S_{1/2}) + Xe^+(^2P_{1/2}$ and $^2P_{3/2})$, is thirteen. Nevertheless, since the incident channel $|X, \Omega = 0^+\rangle$ is† fully symmetric under all symmetry operations of the quasi-molecule, it leads to simplifying selection rules (see also Shakeshaft and Macek 1972). Only the $|A, \Omega = 0^+\rangle$, $|B, \Omega = 0^+\rangle$ and the $|A, \Omega \neq 0\rangle$, $|B, \Omega \neq 0\rangle$ states that are symmetric under reflection in the collision plane have then to be considered. This reduces the problem to only seven states. In addition, since it is predicted (Kubach and Sidis 1973) and calculated (see §5) that the average probability for direct transitions from the state X to the $|A$ or $B, \Omega \neq 0\rangle$ states is small, one can further reduce the problem to the three lowest X, A, $B(\Omega = 0^+)$ states‡. Of course, secondary transitions ($\Omega = 0^+ \leftrightarrow \Omega \neq 0$) can still take place within the manifold of states correlated with $H + Xe^+(^2P_{1/2}$ or $^2P_{3/2})$ thus leading to the polarization phenomena investigated by Shakeshaft and Macek (1972). The neglect of such secondary transitions (assumption (i)) might somehow affect the interference patterns in the theoretical cross sections. Nevertheless it is still expected that by taking into account the most important couplings between the $\Omega = 0^+$ states, the three-state model can

† Ω stands for the projection of the total electronic angular momentum along the internuclear axis.
‡ The A and B states were labelled 1 and 2 respectively in the work of Kubach *et al* (1973, 1975).

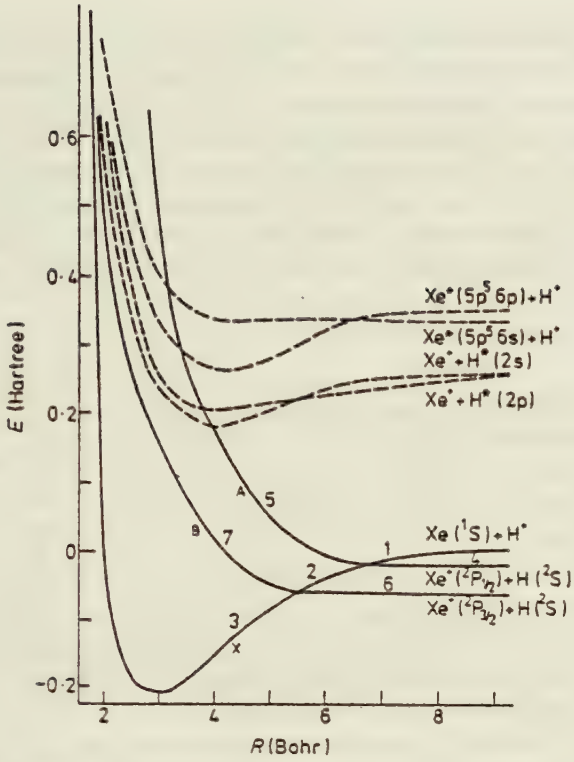


Figure 4. Calculated potential energy curves (Kubach and Sidis 1973). The labelling 1, 2, 3, ..., 7 defines the different portions of the paths used in §§4 and 5. The values 10 and 6·25 Bohr for R_{c1}, R_{c2} are obtained after adjustment of the calculated potential energy difference, at large R, to the experimental energy difference of the atoms.

serve to analyse the main features and the overall trend of the experimental results. It is also worth mentioning that since the important transitions take place at relatively large internuclear distances it would be expensive to attempt the complete close-coupling treatment of a seven-state problem involving a few thousands of partial waves.

In the cross section calculations presented below we have used the molecular data obtained by Kubach and Sidis (1973). The potential energy curves associated with the A and B channels have been shifted upwards by 0·026 Hartree in order to reproduce the experimental energy separations (X–A, B) at large internuclear distances. This adjustment results in an outward shift of the crossing radii, which are then located at $R_{c1} \simeq 10$ Bohr and $R_{c2} \simeq 6$ Bohr. It is assumed that the relevant couplings between the states considered are not significantly affected by such a procedure (assumption (ii)). According to Kubach and Sidis (1973), the most important X–A, X–B couplings arise from the off-diagonal matrix elements of the molecular electronic Hamiltonian (including spin–orbit interaction). Thence the X–A and X–B dynamical radial couplings will be neglected (assumption (iii)). Furthermore, the electronic Hamiltonian being diagonalized within the two-fold subspace spanned by the states $|A, \Omega = 0^+\rangle$ and $|B, \Omega = 0^+\rangle$, we will assume that the transitions between these states are *only virtual transitions* via the X state (assumption (iv) consisting of the neglect of the $\langle A|d/dR|B\rangle$ coupling).

The above approximations define the simplest minimal molecular basis set for treating the near-resonant charge-transfer processes of the $H^+ + Xe$ system. Another

simplifying assumption that can be made would consist of neglecting the virtual transitions from channel A to channel B and in only considering the transitions that take place around the X–A and X–B curve crossings (figure 4). The latter approximation is the basis of the LZS treatment described in §4.1. Account of the virtual (A ↔ X ↔ B) transitions as well as of transitions occurring outside the crossing radii is taken (within assumptions (i) to (iv)) in the quantal calculations described in §4.2. Comparison with experiment at τ values below 600 eV deg, where effects of other inelastic processes are negligible will show the extent of validity of the above approximation.

4. Theory

The scattering amplitudes for the charge-exchange process into $H + Xe^+(^2P_{1/2,3/2})$ are expressed using a partial-wave expansion as:

$$f_{XI}(\theta) = \frac{1}{2i(k_X^{1/2} k_I^{1/2})} \sum_{l=0}^{\infty} (2l + 1)\, S_{XI}^l\, P_l(\cos\theta) \tag{1}$$

where the index X corresponds to the incident channel and I is one of the final channels ending at H(1s) + Xe^+ in a given sublevel. If J designates the electronic angular momentum and J_z its projection on the internuclear axis having Ω as eigenvalue, the above expression is correct for transitions from a state having $J = 0$ (and $\Omega = 0$) to states having $\Omega = 0$ which is the case here.

The scattering matrix elements S_{XI}^l involved in the above expression were obtained for transitions between the lowest $|\Omega = 0^+\rangle$ states of the $(XeH)^+$ system as described below.

4.1. LZS–JWKB formulation

In the Landau–Zener–Stueckelberg approximation transitions occur at the molecular curve crossings. Elsewhere the system is assumed to be unperturbed and it evolves with a given probability on each of the diabatic potentials. Consequently outside of the crossing points only JWKB phases are developed along these potentials. Considering only the three lowest $|\Omega = 0^+\rangle$ states of the $(XeH)^+$ system, which we label X, A and B (figure 4), a column of the scattering S matrix can be written as:

$$[S] = M_{in}\, M_{out} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \tag{2}$$

where in the right-hand side M_{in} and M_{out} are (3 × 3) matrices describing respectively the evolution of the system from infinity to the turning points and from the turning points to infinity. The unit column vector represents the probability amplitudes prior to the collision. The matrices involved in equation (2) are described in the appendix. One obtains, for each partial wave l, the following matrix elements

$$\begin{aligned} S_{XX}^l = \exp(2i\delta_1^l)\{&P_{1l}^{XA} P_{2l}^{XB} \exp[2i(\delta_2^l + \delta_3^l)] + P_{1l}^{XA}(1 - P_{2l}^{XB}) \\ &\times \exp[2i(\delta_2^l + \delta_7^l - \nu_2^l)] + (1 - P_{1l}^{XA}) \exp[2i(\delta_5^l - \nu_1^l)]\} \\ S_{XA}^l = [P_{1l}^{XA}(1 - P_{1l}^{XA})]^{1/2} &\exp[i(\delta_1^l + \delta_4^l)]\{P_{2l}^{XB} \exp[i(2\delta_2^l + 2\delta_3^l + \nu_1^l)] \\ &+ (1 - P_{2l}^{XB}) \exp[i(2\delta_2^l + 2\delta_7^l + \nu_1^l - 2\nu_2^l)] - \exp[i(2\delta_5^l - \nu_1^l)]\} \end{aligned} \tag{3}$$

$$S^l_{XB} = [P^{XA}_{1l} P^{XB}_{2l}(1 - P^{XB}_{2l})]^{1/2} \exp[i(\delta^l_1 + \delta^l_2 + \delta^l_6)] \{\exp[i(2\delta^l_3 + \nu^l_2)] - \exp[i(2\delta^l_7 - \nu^l_2)]\}$$

where P^{XI}_{Ml} is the Landau–Zener probability for remaining on either the X or the I potential at their crossing point R_{cM} and where δ^l_i is the JWKB phaseshift developed along the portion i of the potential (figure 4). These phases are easily expressible as sums of the phases $\phi_I|^R_R$ described in the appendix. Since we consider that the crossings R_{c1} and R_{c2} act independently (Nikitin 1968, Delvigne and Los 1973, Kubach *et al* 1975) we can use for the additional phases ν^l_1 and ν^l_2 the suggested formula (Nikitin and Reznikov 1972, Kotova and Ovchinnikova 1971, Child 1971)

$$\nu^l_i = \tfrac{1}{4}\pi + \gamma^l_i \ln \gamma^l_i - \gamma^l_i + \arg \Gamma(1 + i\gamma^l_i) \tag{4}$$

where γ^l_i is the usual LZS parameter involved in P^{XI}_{Ml} and where Γ is the generalized factorial. This formula shows that ν^l_i vanishes when the turning point coincides with the crossing point. Yet it is known that in this limit the LZS treatment has to be taken with caution. On the other hand when γ^l_i is small ν^l_i tends to the value $\frac{1}{4}\pi$ of the distorted-wave approximation. This constant value has been assumed in our calculations.

It is seen from equations (3) that, when P^{XB}_{2l} is small (as is the case at $E = 18{\cdot}2$ eV) the introduction of a constant phase ($\nu^l_1 = \nu^l_2$) modifies neither the $^2P_{1/2}$ cross section nor the elastic cross section except at small angles corresponding to impact parameters $b > R_{c2}$.

4.2. Integration of the quantal close-coupled equations

The system of coupled equations involved in our problem, for each partial wave l, can be written

$$\left[1\frac{d^2}{dR^2} + \left(k^2 - 2\mu U(R) - 1\frac{l(l+1)}{R^2}\right)\right] F^l(R) = 0 \tag{5}$$

where $\boldsymbol{k}$ is the diagonal matrix of wavenumbers. The diagonal and off-diagonal elements of the symmetric $\boldsymbol{U}$ matrix represent respectively the potentials and couplings (Kubach *et al* 1975, Kubach 1974) which both vanish at infinite R. $F^l(R)$ is the matrix of the linearly independent solutions of the equations.

To solve these equations we have used two procedures:

(i) the Numerov algorithm which consists of a numerical integration with a constant step (Lane and Geltman 1967, Evans *et al* 1971, Evans and Lane 1973). The size of the step depends on the collision energy and is chosen equal to $\lambda/20$, λ being the smallest of the asymptotic wavelengths. The number of steps involved is the main limitation for small λ and for large numbers of partial waves currently involved in atomic collisions at low and moderate energies.

(ii) the 'piecewise analytic method' of Gordon (1969, 1971) which makes use of variable and energy-independent integration steps. This method has proved to be much faster than the Numerov algorithm.

In both cases (i) and (ii) the integration is carried out until a sufficiently large R at which the solutions are matched to the spherical Bessel and Neumann functions in the usual way (Lane and Geltman 1967). This enables the extraction of the S matrix.

The computational details for the procedure (i) have been given elsewhere (Kubach *et al* 1975, Evans *et al* 1971). The procedure (ii) was achieved using a version by Stern *et al* (1975) of the computer program written by Gordon (1971).

4.3. Results

The calculated differential cross sections for electron capture into $H + Xe^+(^2P_{1/2}, ^2P_{3/2})$ at $E = 18{\cdot}2$ eV are shown in figure 5(*a*), together with the elastic cross section. We have found that the elastic result obtained by the numerical integration procedure (Kubach *et al* 1975), for 1000 partial waves, is in good agreement with that obtained by the method of Gordon (1969, 1971). It should be noted that the charge-exchange cross sections do not exhibit the angular threshold encountered in other curve-crossing processes. The $^2P_{1/2}$ oscillations are in phase opposition with the elastic structures whereas the $^2P_{3/2}$ oscillations have a much larger frequency. These features will be analysed in § 5. As estimated by Shakeshaft and Macek (1972), the $^2P_{1/2}$ process has, on the average, a higher cross section than the $^2P_{3/2}$ process at this low energy.

The LZS results at the same energy (figure 5(*b*)) show that the cross-section for $^2P_{3/2}$ process is much smaller than that obtained from the quantal calculation. This arises from the small value of P_{2l}^{XB} which is less than 10^{-2}. In such a case the derivation of the LZS formula breaks down (Thorson *et al* 1971) and the errors introduced by the model are expected to be very important. Although other important discrepancies appear in the comparison of quantal and LZS results for the $^2P_{3/2}$ process, the smallness of its cross section in both calculations results in negligible

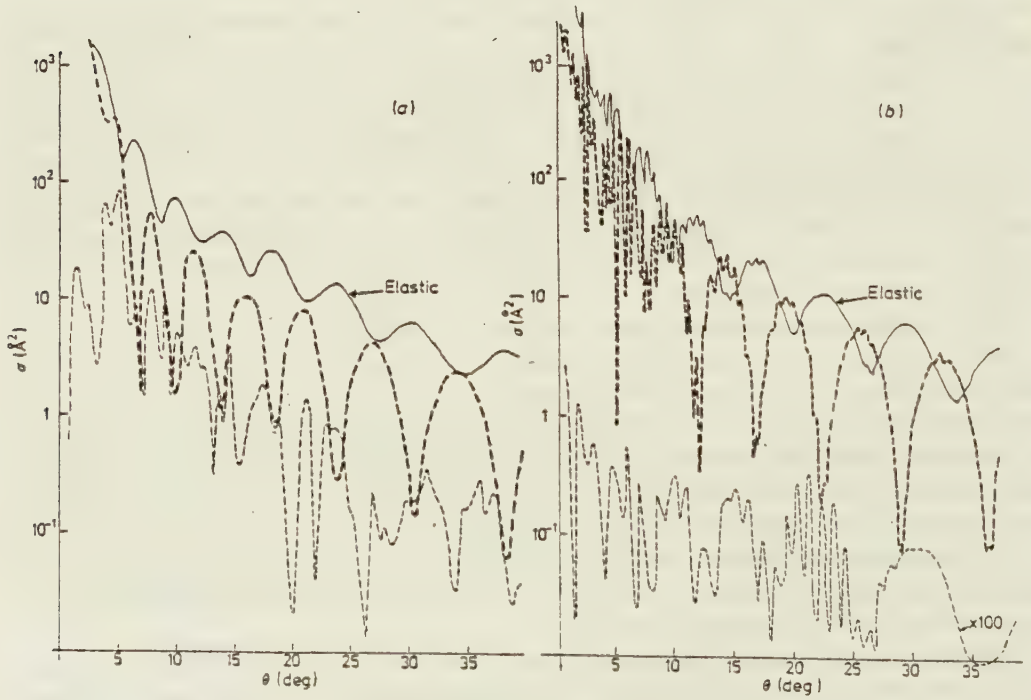


Figure 5. Theoretical differential cross sections at $E = 18{\cdot}2$ eV. (*a*) Quantal results; (*b*) LZS–JWKB result. The thick and thin lines refer respectively to the $^2P_{1/2}$ and the $^2P_{3/2}$ charge-excharge cross sections.

effects on both the elastic and the $^2P_{1/2}$ results. The latter cross section is very similar to that obtained by the quantal procedure. The difference between the two is mainly a phaseshift already discussed (Kubach *et al* 1975) for the elastic cross sections.

The LZS reduced cross sections for charge exchange into $H + Xe^+(^2P_{1/2}, ^2P_{3/2})$ at energies $E = 100$, 200 and 400 eV are plotted together with experiment in figures 6, 7(*a*) and 9 respectively. The results are shown for reduced angles $\tau \leqslant 600$ eV deg only since at larger values of τ other inelastic processes, not taken into account in our calculation, are expected to strongly perturb the charge exchange into the two lowest states. At first sight the comparison of the LZS results with experiment is rather discouraging. As a general remark, the LZS calculation substantially underestimates the $^2P_{3/2}$ cross section (ρ_B) at the lowest energies. However, the results obtained from $E = 18{\cdot}2$ eV to $E = 400$ eV show that this tendency decreases with the increase of the $^2P_{3/2}$ cross section as energy increases. At high energies, the crossing R_{c2} is less 'adiabatic' and better conditions are met to apply the LZS formula. Furthermore the energy increase widens the transition region (Bates 1960) which should beneficially account here for part of the transitions that are not sharply localized around the crossing radii. Notwithstanding the above underestimation, the *shape* of the $^2P_{3/2}$ cross section is seen to fit the corresponding experimental result (ρ_B) better than the $^2P_{1/2}$ cross section (ρ_A) does. The smoothness of the experimental $^2P_{3/2}$ cross section as compared with the corresponding theoretical results can be attributed to a convolution effect introduced by the finite angular resolution of the apparatus (see below). As may be seen by inspection of figures 6 and 7(*a*), the wider low-frequency oscillations in the $^2P_{3/2}$ LZS cross sections also seem to have their counterpart, although less pronounced, in the experimental data.

The cross sections resulting from quantal calculations at $E = 200$ eV (for 2000 partial waves) are shown along with the experimental curves in figure 7(*b*). Again

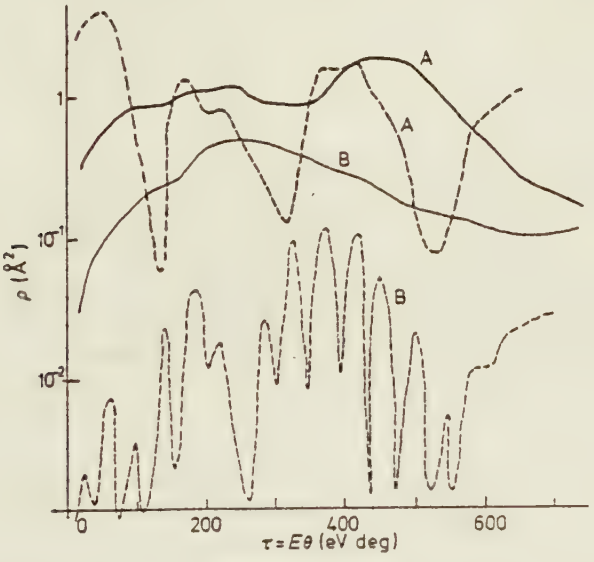


Figure 6. Reduced differential cross sections at $E = 100$ eV. Full curves: experiment; broken curves: LZS–JWKB results. The experimental results for the $^2P_{1,2}$ cross section are arbitrarily normalized to theory at $\tau = 400$ eV deg. The thick and thin lines refer respectively to the $^2P_{1/2}$ and the $^2P_{3/2}$ cross sections.

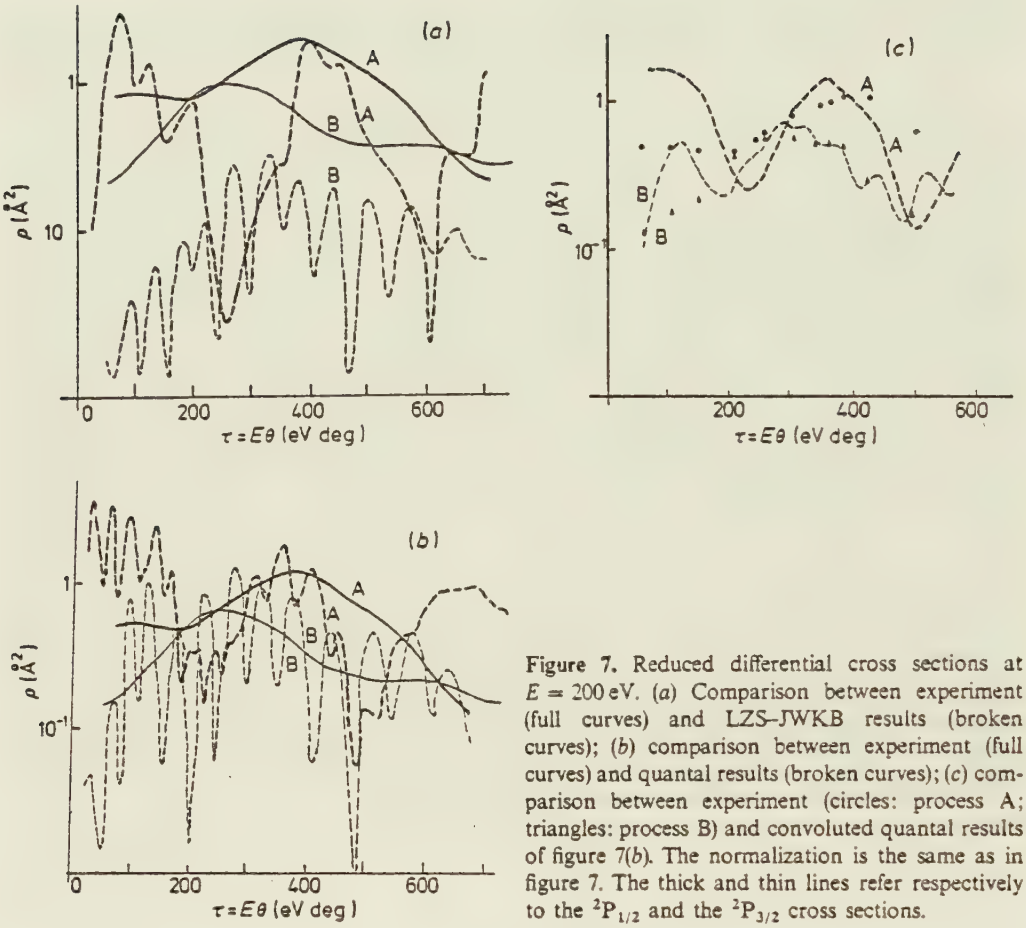


Figure 7. Reduced differential cross sections at $E = 200$ eV. (*a*) Comparison between experiment (full curves) and LZS–JWKB results (broken curves); (*b*) comparison between experiment (full curves) and quantal results (broken curves); (*c*) comparison between experiment (circles: process A; triangles: process B) and convoluted quantal results of figure 7(*b*). The normalization is the same as in figure 7. The thick and thin lines refer respectively to the $^2P_{1/2}$ and the $^2P_{3/2}$ cross sections.

the superposition of high- and low-frequency oscillations are seen in the computed cross sections. For a clearer comparison with experiment, the theoretical data have also been convoluted over angle by using a Gaussian function having a 0·2 deg full width at half maximum. The result is shown in figure 7(*c*) together with the experimental data points normalized to theory at $\tau \simeq 400$ eV deg. The quantal treatment is seen to considerably improve the agreement with experiment. The $^2P_{3/2}$ cross section is indeed strongly enhanced as compared with the LZS results and the ratio of the $^2P_{3/2}$ cross section to the $^2P_{1/2}$ cross section is better reproduced in shape (see figure 8).

Total cross sections for electron capture into the two lowest states have been calculated by integration of the differential cross sections in the range $0 \leqslant \tau \leqslant 600$ eV deg. The results are compared to the data of Koopman in table 1. Good agreement with experiment is found at the lowest energies. The non-negligible $^2P_{3/2}$ population (for instance 17% of the total charge exchange at $E = 200$ eV) should be stressed. Part of the observed discrepancies at higher energy (400 eV) might arise from our neglect of electron-capture processes into higher states as demonstrated by the importance of these processes in the experimental results (figure 3).

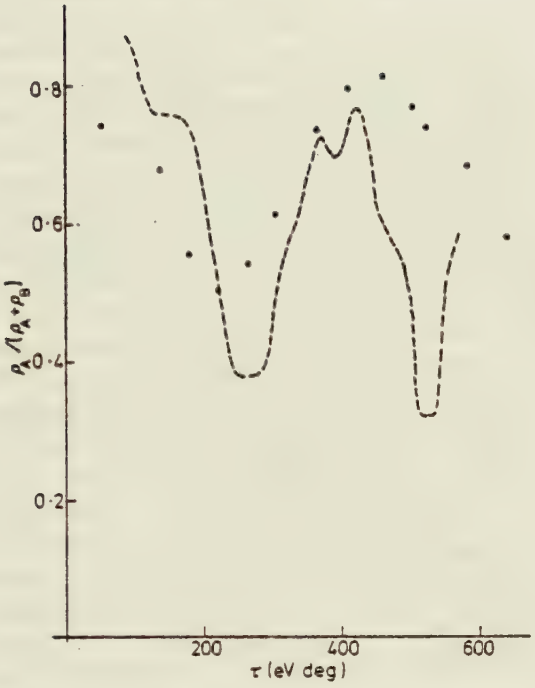


Figure 8. The $\rho(^2P_{1/2})/(\rho(^2P_{3/2}) + \rho(^2P_{1/2}))$ ratio as a function of the reduced angle τ at $E = 200$ eV. Broken curve: data from figure 7(*c*); dots: experimental data points.

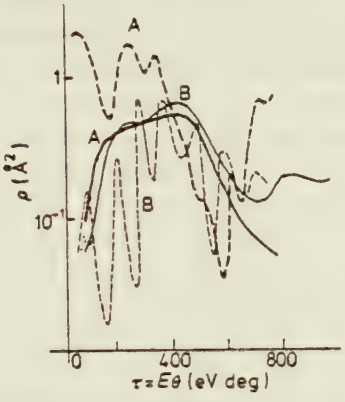


Figure 9. Reduced differential cross sections at $E = 400$ eV (same normalization and caption as in figure 6). The thick and thin lines refer respectively to the $^2P_{1/2}$ and the $^2P_{3/2}$ cross sections.

Table 1. Total cross sections for charge exchange.

Energy (eV)	Present work (Å²)			Koopman (Å²) Experimental total charge exchange
	$^2P_{1/2}$	$^2P_{3/2}$	Sum	
100 (a)	39	0·1	39·1	41
200 (a)	32·1	1·1	33·2	39
(b)	27·2	5·7	32·9	
400 (a)	23·7	2·4	26·1	38

(a) LZS-JWKB results. (b) Quantal results.

5. Discussion

Let us now draw some conclusions from the above triple comparison between the three-state LZS and quantal results and experiment. From table 1 it is seen that both the LZS and the quantal treatments account for the correct order of magnitude of the total near-resonant charge-transfer process to which the $^2P_{1/2}$ cross section contributes most. From the calculations at $E = 200$ eV (figures 7(*b*), (*c*) and 8) it appears that, although discrepancies are seen in some details, some success has been obtained with the three-state quantal treatment in reproducing both the general shape and the relative importance of the $^2P_{1/2}$ and $^2P_{3/2}$ processes. This indicates that we have chosen the most significant interactions involved in the near-resonant charge-transfer process of the $H^+ + Xe$ system. Another aspect of the present theoretical approach which deserves attention is that both the LZS and the quantal treatments yield the same structures (although slightly phase-shifted) in the differential cross sections. These structures, which are only roughly sketched, namely in the $^2P_{1/2}$ experimental cross section, reflect the underlying reality of localized transitions around the crossing radii. This remark in turn allows the understanding of these structures as being produced by the interference between waves scattered by the different branches of the potentials inside the curve crossings. In order to analyse the nature of the oscillations in the differential cross section we have plotted in figure 10 the reduced classical deflection functions $E\theta$ associated with the $^2P_{1/2}$ and $^2P_{3/2}$ channels.

For the $Xe^+(^2P_{3/2})$ process the deflection function is made of two branches associated with the paths 1,2,7–7,6 and 1,2,3–3,6 of figure 4. An extremum is seen at $\tau = E|\theta| \simeq 417$ eV deg. At larger values of τ two impact parameters contribute to the same angle and give rise to Stueckelberg-type interferences. For $\tau \leqslant 417$ eV deg

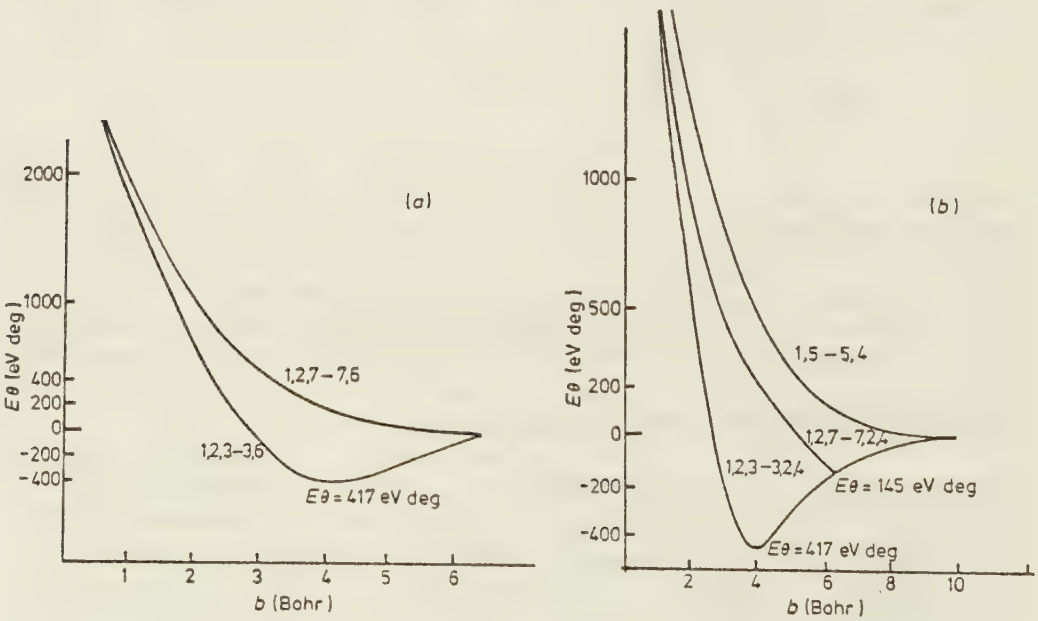


Figure 10. Classical reduced deflection functions ($E\theta$) plotted against impact parameter b for the production of the (*a*) $^2P_{3/2}$, (*b*) $^2P_{1/2}$ states of Xe^+. The labels refer to the paths of figure 4.

four impact parameters are related to the same angle and a mixture of rainbow and Stueckelberg oscillations is produced. For the $Xe^+(^2P_{1,2})$ process and deflection function is made of three branches associated with the paths 1,5–5,4; 1,2,7–7, 2,4 and 1,2,3–3,2,4. Contrary to the $Xe^+(^2P_{3/2})$ case each branch is weighted by a different probability i.e. $P_1^{XA}(1-P_1^{XA})$, $P_1^{XA}(1-P_1^{XA})(1-P_2^{XB})^2$, $P_1^{XA}(1-P_1^{XA})(P_2^{XB})^2$. At low energy (18·2 eV) P_2^{XB} is small and the situation is analogous to the $Xe^+(^2P_{3/2})$ case except that the rainbow angle lies at $\tau \simeq 145$ eV deg. At collision energies of a few hundred eV, P_2^{XB} is no longer negligible and six impact parameters may contribute to the same angle $\tau \lesssim 145$ eV deg. For larger values of τ the situation is again analogous to the $Xe^+(^2P_{3/2})$ case with different weightings of the contributing branches. The occurrence of the A and B processes at angles as small as zero degrees is readily understood by inspection of figure 10.

Figure 10(*b*) also shows that if, as expected from figure 4, the excited molecular states are populated at impact parameters $b \lesssim 4$ Bohr the absorption effects will affect the $^2P_{1/2}$ cross section at reduced angles $\tau \geqslant 500$ eV deg, as is actually seen in the experiment. In addition, for impact parameters $b \leqslant 4$ Bohr the flux that feeds the excited channels ($H^+ + Xe^*$, $H^* + Xe^+$, $H + Xe^{+*}$) comes half from the inward motion of the system along the potential curve associated with channel A and half from the outward motion along the curves associated with the excited channels C, D, etc. Furthermore, since the excited curves are 'rather flat' (or slightly attractive) their contribution to the deflection function will be small compared to that of the strongly repulsive A curve. Consequently, the angular threshold of processes C, D, etc will be located around half the τ value that characterizes the fall-off in the $^2P_{1/2}$ cross section (see figure 3).

The comparison between theory and experiment is rather encouraging in view of the simplicity of the considered three-state models. However this optimism should not hide the significance of the discrepancies observed. Obviously the observed defects of the theoretical results arise from the set of assumptions made in §3 together with the more or less good quality of the molecular properties (e.g. assumption (ii) of §3, see also Kubach and Sidis 1973, Kubach *et al* 1975) involved in the calculations. As an example let us consider the neglect of rotational coupling (assumption (i)). A four-state quantal calculation including the interaction of the channel† $|A, \Omega = 1\rangle$ with the incident channel $|X, \Omega = 0^+\rangle$ demonstrates (figure 11) that the direct $|X, \Omega = 0^+\rangle - |A, \Omega = 1\rangle$ transition is negligible. However, preliminary calculations show that, if allowance is made for the long-range interaction between e.g. the $|A, \Omega = 0^+\rangle$ and the $|A, \Omega = 1\rangle$ states, the sharing between these states favours the $|A, \Omega = 1\rangle$ channel as was found by Shakeshaft (1972). Nevertheless, the sum of the probabilities for populating both the $|A, \Omega = 0^+\rangle$ and the $|A, \Omega = 1\rangle$ states is the same as the probability obtained by neglecting the rotational coupling. This is again related to the smallness of a direct transition between the $|X, \Omega = 0^+\rangle$ and the $|A, \Omega = 1\rangle$ states. Yet the effect of additional transitions (due to rotational or radial dynamical interaction), although small, might affect the structures in the cross section by reducing the amplitude of the oscillations as is seen (e.g. for the $^2P_{1/2}$ results) when going from the LZS treatment to the quantal treatment.

As a concluding remark we would say that the next step in improving the three-state approximation would be to take full account of the neglected d/dR coupling

† The state actually considered is symmetric under reflection in the collision plane and writes as a half and half mixture of the $|A, \Omega = +1\rangle$ and the $|A, \Omega = -1\rangle$ states (Knudson and Thorson 1965).

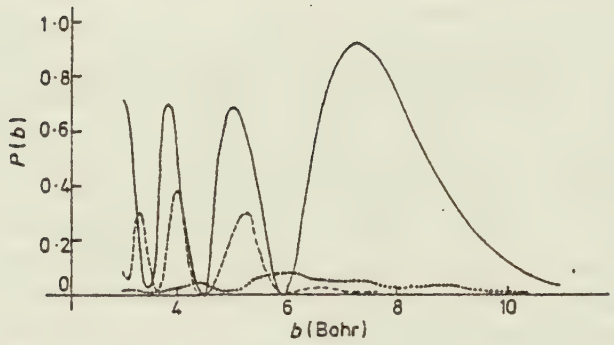


Figure 11. Quantal transition probabilities as functions of impact parameter b obtained at $E = 300$ eV by considering, in addition to the three states $\Omega = 0^+$ (full and broken curves, the $|\Lambda\Omega = 1\rangle$ channel: dotted curve. Note the smallness of the transition probability for populating the latter additional state.

(assumptions (iii) and (iv)), as has recently been performed by Kubach and Sidis (1976) and Benoît *et al* (1976) in the case of the $H^+ + Kr$ charge-transfer problem. Such an improvement might allow determination of which of the neglected radial or rotational coupling is responsible for defects of the present calculations. In any case rotational coupling must be taken into account in polarization studies as e.g. spin polarization (Shakeshaft and Macek 1972) polarization of the emitted light (Vassilev *et al* 1975) and intramanifold transitions (Mies 1973).

Acknowledgments

We are indebted to J C Brenot, J Durup, E Pollack, J P Gauyacq and B Stern for their assistance during the early stage of this work.

Appendix

According to Bobashev (1972), the matrix M_{in} can be written as

$$M_{in} = A|_{R_T}^{R_{c2}} P_2 \cdot A|_{R_{c2}}^{R_{c1}} \cdot P_1 \cdot A|_{R_{c1}}^{\infty}$$

with

$$A|_{R'}^{R} = \begin{pmatrix} \exp(i\phi_X|_{R'}^{R}) & 0 & 0 \\ 0 & \exp(i\phi_A|_{R'}^{R}) & 0 \\ 0 & 0 & \exp(i\phi_B|_{R'}^{R}) \end{pmatrix}$$

$$A|_{R_T}^{R_{c2}} = \begin{pmatrix} \exp(i\phi_X|_{R_{TX}}^{R_{c2}}) & 0 & 0 \\ 0 & \exp(i\phi_A|_{R_{T1}}^{R_{c2}}) & 0 \\ 0 & 0 & \exp(i\phi_B|_{R_{T2}}^{R_{c2}}) \end{pmatrix}$$

$$P_1 = \begin{pmatrix} (P_1^{XA})^{1/2} & (1 - P_1^{XA})^{1/2} e^{iv_1} & 0 \\ -(1 - P_1^{XA})^{1/2} e^{-iv_1} & (P_1^{XA})^{1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$P_2 = \begin{pmatrix} (P_2^{XB})^{1/2} & 0 & (1 - P_2^{XB})^{1/2} e^{iv_2} \\ 0 & 1 & 0 \\ -(1 - P_2^{XB})^{1/2} e^{-iv_2} & 0 & (P_2^{XB})^{1/2} \end{pmatrix}$$

In these formulae $\phi_I|_{R'}^{R}$ is the semiclassical phase developed along the potential I between the points R' and R; P_M^{XJ} has been defined in the text (§4.1). R_{TI} is the turning point on the potential I, and v_I is the additional phase discussed by Thorson *et al* (1971), Child (1971) and Nikitin and Reznikov (1972).

Using the same notation as for M_{in} one has:

$$M_{out} = A|_{R_{e1}}^{\infty} . \bar{P}_1 . A|_{R_{e2}}^{R_{e1}} . \bar{P}_2 . A|_{R_T}^{R_{e2}}$$

where $\bar{P}_M$ is the transposed matrix of P_M.

References

Abignoli M, Barat M, Baudon J, Fayeton J and Houver J C 1972 *J. Phys. B: Atom. Molec. Phys.* **5** 1533–53

Barat M and Lichten W 1972 *Phys. Rev.* A **6** 211–29

Bates D R 1960 *Proc. R. Soc.* A **257** 22–31

Benoît C, Brenot J C, Pommier J, Barat M and Pollack E 1974 *J. Phys. B: Atom. Molec. Phys.* **7** L424–6

Benoît C, Kubach C, Sidis V, Pommier J and Barat M 1976 *J. Phys. B: Atom. Molec. Phys.* submitted for publication

Brenot J C, Pommier J, Dhuicq D and Barat M 1975a *J. Phys. B: Atom. Molec. Phys.* **3** 448–59

Brenot J C, Dhuicq D, Gauyacq J P, Pommier J, Sidis V, Barat M and Pollack E 1975b *Phys. Rev.* A **11** 1245–66

Bobashev S V 1972 *Proc. 7th Int. Conf. on Physics of Electronic and Atomic Collisions* ed T R Govers and F J de Heer (Amsterdam: North Holland) Progress Reports and Invited Papers pp 38–64

Child M S 1971 *Molec. Phys.* **20** 171–84

Delvigne G A L and Los J 1973 *Physica* **67** 166–96

Evans S A, Cohen T S and Lane N F 1971 *Phys. Rev.* A **4** 2235–48

Evans S A and Lane N F 1973 *Phys. Rev.* A **8** 1385–96

Filippenko L G 1960 *Sov. Phys.–Tech. Phys.* **5** 52–7

Fleischmann H H and Young R A 1967 *Phys. Rev. Lett.* **19** 941–3

Gordon R G 1969 *J. Chem. Phys.* **51** 14

——1971 *Meth. Comput. Phys.* **10** 81–109

Jaecks D, Van Zyl B and Geballe R 1965 *Phys. Rev.* A **137** 340–6

Knudson K and Thorson W R 1970 *Can. J. Phys.* **48** 313–29

Kotova L P and Ovchinnikova M Y 1971 *Sov. Phys.–JETP* **33** 1092–8

Koopman D W 1967 *Phys. Rev.* **154** 79–85

Kubach C 1974 *Thèse 3e Cycle* Université Paris VI

Kubach C and Sidis V 1973 *J. Phys. B: Atom. Molec. Phys.* **6** L289–93

——1976 *Phys. Rev.* A to be published

Kubach C, Sidis V and Durup J 1975 *J. Phys. B: Atom. Molec. Phys.* **8** 1129–38

Lane N F and Geltman S 1967 *Phys. Rev.* **160** 53–67

Massey H S W 1949 *Rep. Prog. Phys.* **12** 248–53
Mies F H 1973 *Phys. Rev.* A **7** 942–57
Nikitin E E 1968 *Chemische Elementarprozesse* ed H Hartman (Berlin: Springer Verlag) pp 43–77
Nikitin E E and Reznikov A I 1972 *Phys. Rev.* A **6** 522–3
Rapp D and Francis W E 1962 *J. Chem. Phys.* **37** 2631–45
Sauers T and Thomas E W 1974 *Rev. Sci. Instrum.* **6** 809–13
Shakeshaft R 1972 *J. Phys. B: Atom. Molec. Phys.* **5** 559–70
Shakeshaft R and Macek J 1972 *Phys. Rev.* A **6** 1876–85
Stedeford J B and Hasted J B 1955 *Proc. R. Soc.* A **227** 466
Stern B, Gauyacq J P and Sidis V 1975 *Proc. 9th Int. Conf. on Physics of Electronic and Atomic Collisions, Seattle* (Seattle: University of Washington) and to be published
Thorson W, Delos J B and Boorstein 1971 *Phys. Rev.* A **4** 1052–66
Vassilev G, Rahmat G, Slevin J and Baudon J 1975 *Phys. Rev. Lett.* **34** 444–7
Weise H P, Mittmann H P, Ding A and Henglein A 1971 *Z. Naturf.* **26a** 1112–28

DISCUSSION ET COMMENTAIRES

1. Polarisation des atomes d'hydrogène produits par échange de charge quasi-résonnant dans les collisions $H^+ + Xe$.

Shakeskaft et Macek /31/ ont montré que l'échange de charge quasi-résonnant dans les collisions $H^+ + Xe$ (et $H^+ + Kr$) pouvait conduire à la formation d'atomes d'hydrogène à spin polarisé par rapport au plan de la collision. Nous montrons ici comment l'on peut interpréter ce phénomène dans la description moléculaire de l'échange de charge dans la collision $H^+ + Xe$, en nous limitant aux cas où l'on peut négliger la production de Xe^+ dans l'état $^2P_{3/2}$. Le produit de l'échange de charge dans la collision $H^+ + Xe$, c'est-à-dire $Xe^+(^2P_{1/2}) + H\,(^2S_{1/2})$ correspond à une dégénérescence d'ordre 4. Les états dégénérés peuvent être repérés par les valeurs du moment cinétique électronique total J (0 ou 1) et de sa projection M_J sur l'axe internucléaire Oz. Les vecteurs $|\,J, M_J\rangle$ s'écrivent :

$$
\begin{aligned}
|\,1,1\rangle &= \alpha_H\ \alpha_{Xe} \\
|\,1,0\rangle &= \frac{1}{\sqrt{2}}\,(\alpha_H\ \beta_{Xe} + \beta_H\ \alpha_{Xe}) \\
|\,1,-1\rangle &= \beta_H\ \beta_{Xe} \\
|\,0,0\rangle &= \frac{1}{\sqrt{2}}\,(\alpha_H\ \beta_{Xe} - \beta_H\ \alpha_{Xe})
\end{aligned}
\qquad (6)
$$

où α_{Xe}, β_{Xe}, α_H et β_H désignent respectivement les vecteurs propres des opérateurs $(j_z)_{Xe}$ et $(S_z)_H$ agissant sur les moments de Xe^+ et de H avec les valeurs propres $\pm 1/2$.

L'état $|\,0,0\rangle$, de symétrie 0^-, n'est pas produit par la collision $H^+ + Xe$ (cf chapitre IV et réf. /31/). Par contre l'état $|\,1,0\rangle$, de symétrie 0^+, est peuplé par l'intermédiaire du couplage électronique et spin-orbite avec la voie d'entrée corrélée à $Xe + H^+$. Si cet état est le seul peuplé il n'y a pas de polarisation par rapport au plan de collision. En effet, une mesure de la projection du spin de H sur un axe y perpendiculaire au plan

de collision donnera :

$$\langle 1,0 \left| (S_y)_H \right| 1,0\rangle = 0 \qquad (7)$$

où l'intégration est faite sur les coordonnées de spin des électrons
Il faut donc, pour qu'une polarisation existe, que les états $|1,1\rangle$ et $|1,-1\rangle$ soient peuplés. En fait ils ne le sont pas,ou alors très peu par le couplage rotationnel direct avec la voie d'entrée (cf figure 11). Ils peuvent cependant être peuplés de façon appréciable par couplage rotationnel secondaire entre les états $|A,\ \Omega = 0^+\rangle$ et $|A\ ,\ |\Omega| = 1\rangle$ corrélés à $|1,0\rangle$ et $\frac{1}{\sqrt{2}}(|1,1\rangle - |1,-1\rangle)$.

Si ce dernier point est vérifié la partie de la fonction d'onde totale (électronique et nucléaire) correspondant à la formation de Xe^+ $(^2P_{1/2})$ + H à un angle de diffusion θ s'écrira :

$$\Psi(\vec{r}\ ,\ R,\ \theta) \sim \frac{e^{ikR}}{R}\left(\frac{f_1(\theta)}{\sqrt{2}}\{|1,1\rangle - |1,-1\rangle\} + f_0(\theta)\,|1,0\rangle\right) \qquad (8)$$

où $f_1(\theta)$ et $f_0(\theta)$ désignent les amplitudes de diffusion.

Une mesure de la projection du spin de H sur l'axe y,donnera alors :

$$\frac{\langle\Psi|(S_y)_H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{if_0^* f_1 - f_1^* f_0}{\sqrt{2}\,|f_0|^2 + |f_1|^2} = \frac{\sqrt{2}\,|f_0||f_1|\ \sin\Delta}{|f_0|^2 + |f_1|^2} \qquad (9)$$

où f^* désigne le complexe conjugé de f et où Δ représente le déphasage entre f_0 et f_1. Cette expression de la fraction de polarisation a été obtenue par Shakeshaft et Macek /31/.

Ainsi, pour qu'une polarisation par rapport au plan de collision existe, il faut que les amplitudes de diffusion f_0 (θ) et f_1 (θ) et leur déphasage soient non nuls.

Nous cherchons à montrer maintenant que le couplage rotationnel secondaire entre les états $|A,\ \Omega = 0^+\rangle$ et $|A,|\Omega| = 1\rangle$ peut conduire à des transitions non négligeables entre ces états, et assurer ainsi une valeur non nulle à la quantité f_1 (θ) intervenant dans la relation (9). Pour étudier ce phénomène on peut séparer le domaine des distances internucléaires en deux régions : celle pour laquelle le couplage rotationnel est beaucoup

plus petit que la séparation énergétique (R petit) et celle pour laquelle ce couplage devient du même ordre de grandeur, ou plus grand, que la séparation énergétique. Considérons un système évoluant de R petit à R grand et initialement dans l'état $|A, \Omega = 0^+\rangle$: l'état $|A, |\Omega| = 1\rangle$ va pouvoir être peuplé par couplage rotationnel, ceci pour $R \gtrsim R_o$ où R_o est la distance pour laquelle le couplage rotationnel n'est plus négligeable devant la séparation énergétique.

La probabilité de transition s'obtient en résolvant les équations couplées semi-classiques :

$$\frac{dC_0}{dt} = \frac{v_o b \langle J_y \rangle}{R^2} \cdot C_1$$
$$\frac{dC_1}{dt} = -\frac{v_o\, b \langle J_y \rangle}{R^2} \cdot C_0 \qquad (10)$$

où C_0 et C_1 désignent respectivement les amplitudes des états $|A, \Omega = 0^+\rangle$ et $|A\ , |\Omega| = 1\rangle$. On a négligé dans (10) la séparation énergétique, petite pour $R > R_o$, entre les états. Les solutions du système (10) peuvent être cherchées sous la forme /96/:

$$C_0 = \cos\ A\ (t_o\ ,\ t)$$
$$C_1 = -\sin A\ (t_o,\ t) \qquad (11)$$

avec, si l'on néglige la variation de $\langle J_y \rangle$ avec R :

$$A\ (t_o, t) = v_o\ b \langle J_y \rangle \int_{t_o}^{t} \frac{dt'}{R^2} \qquad (12)$$

En utilisant la loi $R\ (t) = \sqrt{b^2 + v_o^2\ t^2}$ de la trajectoire linéaire, on obtient avec les conditions initiales $(t_o\ ,\ R_o)$:

$$\left|C_1\ (\infty)\right|^2 = \sin^2\ (\Pi/2 - \text{arctg}\ \sqrt{R_o^{\,2}/b^2 - 1}) \qquad (13)$$

la probabilité de transition est donc très importante si $R_o \simeq b$.

Dans le cas de la collision H^+-Xe à 100 eV on trouve par exemple $b = 4a_o$, $R_o \simeq 8{,}5a_o$, ce qui donne : $|C_1(\infty)|^2 \simeq 22$ %.

Le couplage rotationnel secondaire conduira donc à des amplitudes de diffusion $f_1(\theta)$ appréciables*. Le déphasage Δ intervenant dans la relation (9) contiendra la différence des phases développées sur les potentiels associés à $|A, |\Omega| = 1\rangle$ et $|A, \Omega = 0^+\rangle$ et, pour $f_0(\theta)$, la phase développée sur l'état X pour $R < R_{c1}$ (cf fig 4). Il n'y a aucune raison pour que Δ soit nul.

2. Règles de sélection pour le double transfert de charge :

Le double transfert de charge dans la collision $H^+ + Xe$:

$$H^+ + Xe \longrightarrow H^- + Xe^{++}$$

a été observé par Fournier et al /97/

On peut appliquer la règle, utilisée par Shakeshaft et Macek /31/, de la conservation des propriétés de symétrie du système par réflexion dans le plan de collision, pour éliminer certains états correspondant à la configuration : $5p^4$ de Xe^{++}. L'état initial du système (H^+ + Xe) étant symétrique par rapport au plan de collision ; l'état final devra être également symétrique. Cette règle n'exclut que la composante 0 de l'état $^3P_1$ de Xe^{++}. En fait, si l'on se limite à des états de symétrie 0^+, on peut éliminer toutes les composantes de cet état $^3P_1$ qui, effectivement, n'apparaît pas sur les spectres de la référence /97/. Les états $^1D_2$, $^1S_0$, $^3P_0$, $^3P_2$ de Xe^{++} ont tous une composante 0^+ et peuvent donc être peuplés. Ces remarques ont primitivement été faites par Fournier et al /97/. Dans les chapitres VII et VIII, nous montrerons comment le double échange de charge dans les états $^1D_2$ et $^1S_0$ de l'ion GR^{++} peut être, du moins partiellement, abordé.

*La détermination précise de $f_1(\theta)$ est difficile puisque le couplage rotationnel secondaire doit avoir lieu, dans notre cas, à l'entrée. (R décroissants) et à la sortie (R croissants).

Chapitre VII

Molecular study of the H^+-Kr collisional system*

C. Kubach

Laboratoire des Collisions Ioniques, associé au Centre National de la Recherche Scientifique, Bât. 420, Université Paris-Sud, 91405 Orsay, France

V. Sidis*

Centre de Mécanique Ondulatoire Appliquée, 23 rue du Maroc, 75019 Paris, France

(Received 21 January 1976)

Ab initio calculations have been performed to provide the basis for a molecular study of the elastic and the lowest charge-transfer channels in $H^+ + Kr$ collisions. The adiabatic ground-state potential-energy curve agrees satisfactorily with that predicted from elastic scattering experiments. In the Hartree-Fock treatment, the charge transfer into $H(1s) + Kr^+(4p^5)$ appears to be mainly caused by a double virtual electronic transition via a doubly excited state. A "projected valence bond" (PVB) treatment involving single-configuration diabatic states built from projected H and Kr atomic orbitals is also presented. With such diabatic states the charge-exchange process is suitably described as occurring directly under the effect of an exponentially decreasing coupling between closely lying and almost parallel energy curves. The defects of the PVB approximation arising at small internuclear distances (R) are discussed. Diabatic states for the spin-orbit coupling are suggested for studying the population sharing between the $\Omega = 0^+$ states dissociating into $H + Kr^+(4p^5: {}^2P_{3/2}, {}^2P_{1/2})$. A procedure involving a basis change from the adiabatic states at small R to the PVB states at large R, together with the diabatic states for spin-orbit coupling is proposed to solve effectively the relevant scattering close-coupling equations.

I. INTRODUCTION

To date, most of our knowledge of the $(H\text{-}Kr)^+$ molecule comes from investigations on the scattering of protons by Kr atoms. With the availability of detailed experimental results on the elastic scattering of protons by rare gases[1,2] it became desirable to have at hand some realistic potentials describing the H^+–rare-gas interactions. For the particular H^+-Kr system the ground-state potential well determined by Moran and Friedman[3] was later used by Helbig and Ferguson[4] to obtain the parameters involved in their analytical potential model. Another type of parametrized analytical potential was proposed by Weise *et al.*,[2] who determined the relevant parameters by a fitting procedure to their experimental elastic cross sections. In addition, a little earlier, Rich *et al.*[5] were able to extract from high-resolution experimental data accurate interatomic potentials for the rare-gas–hydride ions by using an inversion technique.

In the early days of the development of collision spectroscopy Fleischman and Young[6] reported on two distinct features that appeared in their measurements of the charge-transfer cross sections for the scattering of H^+ by Kr at medium energies. These authors tentatively attributed these "anomalies" to a rainbow phenomenon and to curve-crossing effects induced at relatively large internuclear distances (R). It thus appeared desirable that a detailed theoretical analysis be carried out to check further this interpretation. From diabatic correlation diagrams[7,8] such a curve crossing is not expected in the H^+–rare-gas family until the H^+-Xe system is reached. Therefore a quasiresonant charge-transfer mechanism (perturbed symmetric resonance[9] or Demkov model[10]), favored by the small energy gap between the $H^+ + Kr(4p^6)$ and $H(1s) + Kr^+(4p^5)$ channels, is more likely[11] to be at the origin of the second set of observed structures.[6] As complementary information, the known repulsive behavior of the lowest charge-transfer potential in the rare-gas–hydride ions indicates that the rainbow feature displayed in the above experimental data is most probably related to the well in the ground-state potential. The recognition that the transition region should be located at large internuclear distances is compatible with the assumptions of a Demkov-type mechanism[10] and it is in accord with the large total charge-exchange cross sections measured by Koopman.[12]

To our knowledge, the first theoretical analysis of the inelastic effects in H^+-Kr collisions was provided by Johnson *et al.*,[13] who phenomenologically developed model potentials and interactions. This approach yielded the value of $R = 7a_0$ for the location of the transition region, as well as qualitative agreement with experiment.[13] Motivated by a research on the collisional production of spin-polarized H atoms, Shakeshaft and Macek[14] performed a theoretical study on the H^+-Kr system. The rapid decrease of their calculated transition probabilities for impact parameters larger than $7a_0$ indeed confirmed the location of the transition region

estimated in Ref. 13. Unfortunately the Herman-Skillman potentials and couplings involved in these calculations were not reported.

In this respect, the potential-energy curves and the nature and the behavior of the coupling terms depend on the type of wave functions used to handle the problem. If the wave functions result from relatively large configuration interaction (CI) calculations, then the radial coupling due to the d/dR operator is the main source of transitions between states having the same symmetries.[15] Even in the single-configuration Hartree-Fock [or self-consistent field (SCF)] description a d/dR coupling appears between two states which differ only by one molecular orbital (MO).[16] It is shown in Sec. II D that cases also arise where potential couplings, induced by off-diagonal matrix elements of the electronic Hamiltonian, are also required. The present paper stresses the importance of these couplings in conjunction with virtual transitions via intermediate molecular states in some cases where SCF-MO's are involved.

Yet a question arises as to how these types of potentials and these coupling schemes can be reconciled with the charge-transfer models that appeared in the literature.[9,10] These models, namely, the one described by Demkov,[10] involve parallel energy curves and an exponentially decreasing potential coupling of the valence-bond exchange-interaction type. The region of internuclear distances important for the transition is that wherein the coupling is of the order of half the resonance energy defect.[17] Such an approach implicitly assumes that the dynamical radial interactions are sufficiently small to be neglected or, in other words, that a diabatic representation is used.[18] Although at present the general definition of diabatic states remains an open problem, we show in Sec. III that the lowest charge-transfer channels in the $(H\text{-}Kr)^+$ system provide a situation where most of the known definitions of diabatic states meet. The projected-valence-bond (PVB) states defined in the present paper indeed satisfy the criterion introduced by Smith[18] and they fit with a suggestion made by O'Malley.[19]

Although the PVB approach has important merits for handling the charge-transfer transition expected at large internuclear distance, it appears from Sec. III that it fails, at small internuclear distances, to properly account for polarization distortion. Such a discrepancy has a dramatic consequence when the correct phases developed along the accessible molecular paths are required to account for the structures in the differential cross sections. It is therefore suggested that a basis change from the "atomic" diabatic PVB basis at large R to the "molecular" adiabatic SCF-CI basis at small R be carried out in order to obtain both the magnitude and the shape of the differential cross sections. The feasibility of such a transformation during the resolution of the quantum-scattering close-coupling equations has already been demonstrated by Stern *et al.*[20]

Furthermore, in order to study the sharing of the transferred electron between the two subchannels $H(1\,^2S_{1/2})+Kr^+(^2P_{3/2})$ and $H(1\,^2S_{1/2})+Kr^+(^2P_{1/2})$,[21] we suggest in Sec. IV the use, in conjunction with the above procedure, of a particular diabatic basis to handle the transitions induced by the spin-orbit coupling.

The results and the methods outlined in the present paper are being currently used in quantum calculations on the elastic and the lowest charge-transfer scattering processes at low and moderate energies. The latter calculations will be presented along with new experimental data in a forthcoming paper.[21]

II. LCAO-MO-SCF APPROACH

A. Technical description

The ground-state single-configuration wave function $(\ldots 8\sigma^2 \ldots 4\pi^4 \ldots 1\delta^4)\,X\,^1\Sigma^+$ of the $(HKr)^+$ molecule has been obtained in the LCAO-STO-MO-SCF (LCAO: linear combination of atomic orbitals; STO: Slater-type orbital) approximation with the help of the ALCHEMY program written by Bagus *et al.*[22] The same atomic basis set of STO's has been used throughout the whole range of internuclear distances R (Table I). The STO set chosen to describe the inner orbitals of Kr, from 1s to 3p, has been taken from the minimal basis set of Clementi and Raimondi.[23] Greater flexibility is

TABLE I. STO basis set used in calculations on the $(KrH)^+$ system.

	ζ	nucleus		ζ	nucleus
1s	35.2316	Kr	4p	1.9621	Kr
2s	13.1990	Kr	4p	1.4220	Kr
2p	16.0235	Kr	4d	0.4600	Kr
3s	7.0109	Kr	4d	1.6000	Kr
3p	6.1884	Kr	4f	0.2500	Kr
3d	5.1913	Kr	5s	0.9100	Kr
3d	3.3498	Kr	5p	0.6100	Kr
3d	7.6895	Kr	1s	1.0950	H
3d	10.3162	Kr	1s	0.5000	H
3d	16.7379	Kr	2s	1.1804	H
4s	3.3810	Kr	2s	2.5623	H
4s	2.5651	Kr	2s	0.5000	H
4s	1.7315	Kr	2p	1.8451	H
4p	5.2590	Kr	2p	0.5000	H
4p	3.0783	Kr	3d	2.7577	H

allowed for the outer orbitals ($4s$, $3d$, and $4p$), which are described with an extended STO set.[24] The Rydberg orbitals of Kr ($5s$, $5p$, and $4d$) were obtained by minimization of the corresponding excited atomic energy levels with respect to variation of the STO exponents. The STO basis on the H atom is that of Peyerimhoff[25] augmented by orbitals which allow for the description of the H ($n=2$) states.

For each value of R, the excited single-configuration wave functions are obtained in the virtual-orbital approximation[26] by electron jumps from the occupied MO's of the ground state to the empty MO's generated in the SCF calculation (virtual orbitals).

To account for the spin-orbit interaction (H_{SO}) the same approximations were done as in the work of Kubach and Sidis.[27] Diagonalization of the total electronic Hamiltonian $H_{el}+H_{SO}$ in the subspace spanned by the first excited $(\ldots 8\sigma^2 9\sigma \ldots 4\pi^4 1\delta^4)\,{}^1\Sigma^+$ state (labeled $I^1\Sigma^+$ hereafter) and the lowest ${}^3\Sigma^+$ and ${}^{3,1}\Pi$ states leads to the energy curves correlated with $H(1^2S)+Kr^+(4p^5\,{}^2P_{1/2}$ and ${}^2P_{3/2})$. Some of these curves are displayed in Fig. 1. Also shown in Fig. 1 are the energy curves of the ground state $X^1\Sigma^+$ and some excited ${}^1\Sigma^+$ states dissociating into

$$H^*(n=2)+Kr^+(4p^5\,{}^2P),\quad H^++Kr^*(4p^5\,5s,\ 5p,\text{ and }4d),$$
$$H^-+Kr^{++}(4p_\pi^4:(\sqrt{2}\,{}^1D+{}^1S)/\sqrt{3})\,.$$

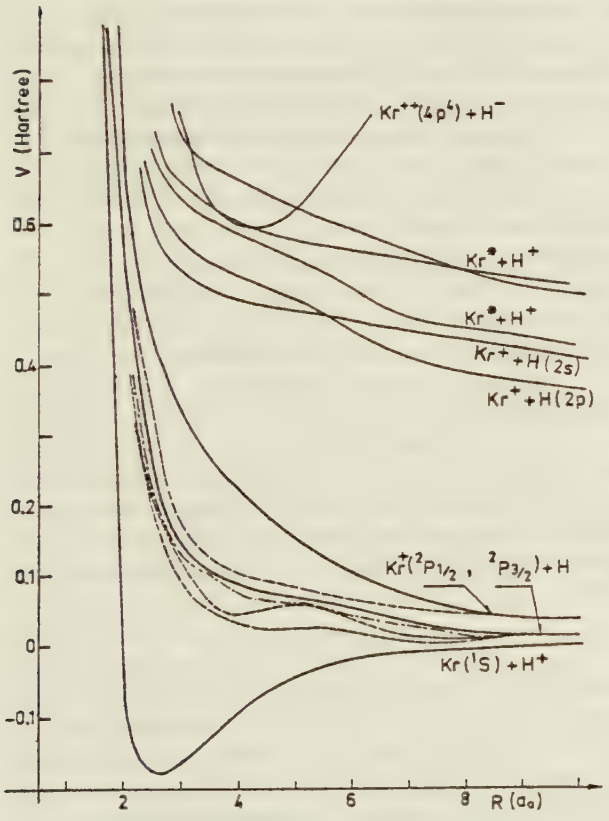


FIG. 1. Some SCF potential-energy curves of the $(Kr-H)^+$ system. The spin-orbit effects are included in the seven lowest curves. ——: $\Omega=0^+$ and ${}^1\Sigma^+$ states; – – –: $\Omega=\pm 1$ states; –·–·–: $\Omega=\pm 2$ state. Energies are measured from the ground-state level of the Kr atom.

B. Ground-state potential

The parameters of the $X^1\Sigma^+$ potential well are reported in Table II and compared with values derived from low-energy elastic-scattering experiments.[2,5] In the low-energy range ($E\leq 40$ eV) the system is expected to follow an adiabatic potential. Thus a valid comparison to the experimental data would involve an adiabatic potential. The adiabatic potential was obtained from a CI involving 28 states of ${}^1\Sigma^+$ symmetry, which are generated by all of the one- and two-electron excitations from the ground-state configuration to virtual orbitals $n\sigma$ ($9\leq n\leq 14$). From Table II slight differences appear between the various potentials when they are compared with each other. Nevertheless the elastic differential cross section[21] involving the adiabatic potential was found to accurately reproduce the experimental data of Champion *et al.*[1] In contrast similar theoretical calculations[21] (for a 15.8-eV collision energy) displayed a small shift when compared with with the experimental results of Weise *et al.*[2] As a tentative explanation of this discrepancy one can think of invoking the perturbative effect induced by inelastic processes.

C. Coupling terms inducing the charge-exchange transitions

Given the small energy defect between the $H^++Kr(4p^6\,{}^1S)$ and $H(1^2S)+Kr^+(4p^5\,{}^2P_{3/2},{}^2P_{1/2})$ levels, the lowest charge-transfer channels are expected to be the main inelastic processes at low and moderate energies. The potential-energy curves of the first excited ${}^{1,3}\Sigma^+$ and ${}^{1,3}\Pi$ states being widely separated from the $X^1\Sigma^+$ level at

TABLE II. Comparison between the experimental and the present calculated parameters for the ground-state potential well of the $(KrH)^+$ system. The parameters of the calculated potentials have been obtained by using a parabolic fit to the calculated energies at $2.5a_0$, $2.7a_0$, and $3.0a_0$.

	Expt.			Calc.	
	Ref. 2		Ref. 5	SCF	SCF-CI
Equilibrium distance (a_0)	2.78	±0.11	2.95	2.66	2.70
Well depth (hartree)	0.1635	±0.004	0.1696	0.1690	0.1764

TABLE III. Comparison of the rotational coupling (calculated for a collision energy of 100 eV) and the spin-orbit coupling with the related energy differences (data are in atomic units, a_0 hartree).

R \ b	$v_0 b\langle {}^1\Pi\|L^+\|X\,{}^1\Sigma^+\rangle/R^2$ 2	4	6	8	10	$E_{{}^1\Pi}-E_{X\,{}^1\Sigma^+}$	$\langle {}^3\Pi\|H_{SO}\|X\,{}^1\Sigma^+\rangle$	$E_{{}^3\Pi}-E_{X\,{}^1\Sigma^+}$
2	1.38×10^{-3}					5.60×10^{-1}	4.8×10^{-4}	5.56×10^{-1}
4	2.78×10^{-3}	5.56×10^{-3}				1.93×10^{-1}	4.06×10^{-3}	1.77×10^{-1}
6	8.1×10^{-4}	1.62×10^{-3}	2.43×10^{-3}			7.95×10^{-2}	2.67×10^{-3}	7.52×10^{-2}
8	1.2×10^{-4}	2.4×10^{-4}	3.6×10^{-4}	4.8×10^{-4}		3.44×10^{-2}	7.7×10^{-4}	3.41×10^{-2}
10	2×10^{-5}	4×10^{-5}	6×10^{-5}	8×10^{-5}	1×10^{-4}	2.99×10^{-2}	2.3×10^{-4}	2.99×10^{-2}

small and medium values of R (see Table III), the charge-transfer transition would most likely take place at relatively large internuclear distances ($R \geq 4a_0$), where the energy curves lie the closest to each other. In addition, the coupling terms inducing these charge-transfer transitions have at large R an essentially exponential decrease. Thus the $(H\text{-}Kr)^+$ system provides a typical example of a perturbed symmetric resonance.[9]

Among the coupling terms capable of inducing these transitions, the direct rotational coupling between the states $(\ldots 8\sigma^2\ldots 4\pi^4\ldots)X\,{}^1\Sigma^+$ and $(\ldots 8\sigma^2 9\sigma\ldots 4\pi^3\ldots)\,{}^1\Pi$ is expressed semiclassically as

$$v_0 b\langle 9\sigma|L^-|4\pi^+\rangle/R^2\,,$$

where v_0 and b are, respectively, the incident nuclear velocity and the impact parameter; L^- is the lowering operator for the orbital electronic angular momentum. For H^+-Kr collisions at an energy of 100 eV this direct rotational coupling is at most (for $R \geq 2a_0$) about two orders of magnitude smaller than the energy difference between the above $X\,{}^1\Sigma^+$ and ${}^1\Pi$ states (Table III). The direct spin-orbit interaction between the $X\,{}^1\Sigma^+$ and $(\ldots 8\sigma^2 9\sigma\ldots 4\pi^3\ldots)\,{}^3\Pi$ states also compares in the same way with the $X\,{}^1\Sigma^+$-${}^3\Pi$ energy difference. Since the Brillouin theorem[28] holds for the $X\,{}^1\Sigma^+$ and $I\,{}^1\Sigma^+$ states only the radial dynamical coupling between these states remains. The dynamical radial coupling, written semiclassically

$$\sqrt{2}\,v_R\langle 8\sigma|d/dR|9\sigma\rangle$$

(v_R being the radial nuclear velocity), is a difficult quantity to calculate. Indeed, in addition to the easy evaluation of d/dR matrix elements between basis STO's, it requires a numerical differentiation of the MO expansion coefficients. This, in turn, necessitates two complete SCF calculations at close internuclear distances R and $R+\delta R$. Such a calculation has been performed only around $R=7a_0$ and $6a_0$, which is the transition region predicted by Johnson *et al.*[13]

The resulting d/dR matrix element yields a dynamical radial coupling of about 0.0045 hartree for a collision energy of 100 eV. This coupling, which amounts to 18% and 10% of the $X\,{}^1\Sigma^+$-$I\,{}^1\Sigma^+$ energy difference, respectively, at $7a_0$ and $6a_0$, seems insufficient to explain by itself the important total cross section for charge transfer observed by Koopman[12] (this is further justified by the results obtained by Benoit *et al.*[21]).

D. Virtual transitions via a doubly excited state

Investigation of the coupling terms induced by the electronic Hamiltonian H_{el} shows that, although according to the Brillouin theorem[28] the $\langle X\,{}^1\Sigma^+|H_{el}|I\,{}^1\Sigma^+\rangle$ matrix element is zero, there are still indirect $X\,{}^1\Sigma^+$-$I\,{}^1\Sigma^+$ interactions involving doubly excited states. In particular both the $X\,{}^1\Sigma^+$ and $I\,{}^1\Sigma^+$ states are found to mainly interact with the state $(\ldots 9\sigma^2\ldots 4\pi^4\ldots)\,D\,{}^1\Sigma^+$** which dissociates into $H^-(1s^2)+Kr^{++}(4p_\pi^4)$. The other doubly excited states (namely, those investigated in the CI calculation) were found to be unimportant for $R \gtrsim 3a_0$. To roughly vizualize how this indirect interaction arises, one can note, for instance, that the $I\,{}^1\Sigma^+$ state perturbed to first order is

$$|g\,{}^1\Sigma^+\rangle = |I\,{}^1\Sigma^+\rangle + \frac{\langle D\,{}^1\Sigma^+|H_{el}|I\,{}^1\Sigma^+\rangle}{E_I - E_D}\,|D\,{}^1\Sigma^+\rangle\,, \quad (1)$$

where E_I and E_D are the diagonal matrix elements of H_{el} for the states $I\,{}^1\Sigma^+$ and $D\,{}^1\Sigma^+$, respectively. This relation shows how the g and X states do interact through the D component. The resulting coupling

$$H_{Xg} = \langle X|H_{el}|D\rangle\langle I|H_{el}|D\rangle\,(E_I - E_D)^{-1} \quad (2)$$

is not negligible compared to the $X-I$ energy difference, and it is more important than all the couplings investigated above. It is worth pointing out that a very analogous situation was found in the study of the $(HXe)^+$ system,[29] where the $|K\,{}^1\Sigma^+\rangle$ state defined there looks very much like the $|g\,{}^1\Sigma^+\rangle$ state of Eq. (1). The above analysis shows that in using a basis of SCF configuration-state functions the charge-transfer process is mainly caused by virtual transitions via the doubly excited $D\,{}^1\Sigma^+$ state.

The charge-transfer mechanism described here differs from the two-state model involved in the perturbed symmetric resonance[9] by the necessity of including a "relay state." However, with such a complicate description it is difficult to decide where the transition takes place or whether it is at all localized. Yet by approximating the perturbed states as in Eq. (1) one finds that the H_{Xf} interaction equals half the $X-I$ energy difference at an internuclear distance $R \simeq 6.5a_0$. This gives an estimate of the distance where the transitions are most likely to occur. The calculated charge-transfer probabilities[21] indeed confirm that the transitions do start below this value of the impact parameter. Another drawback of the above description is that at collision energies smaller than 40 eV the $D^1\Sigma^+$ channel is closed, which considerably complicates the treatment and the understanding of the charge-transfer process. Furthermore, although the $\langle X^1\Sigma^+ | d/dR | I^1\Sigma^+ \rangle$ interaction has been found insufficient to explain the importance of the total charge-transfer cross sections it is still expected to participate in this process. The difficulty of calculating this matrix element, as discussed above, and the complexity it introduces when involved in a quantum-mechanical treatment of the scattering close-coupling equations[30] require that a different approach be used. Also, one can think of reducing the length of the problem by making another choice of molecular basis set where the important interactions are confined to the lowest charge-transfer states only.

III. PVB APPROACH

A. General

Asymmetric diatomic systems involving a very light atom and a very heavy element provide specific cases where diabatic orbitals satisfying the definition of Smith[18] can be defined. Indeed, in such cases the center of mass of the nuclei can be assumed with good accuracy to be located on the heavy atom. Since the d/dR operation is carried out in keeping fixed the electron coordinates as referred to the center of mass of the nuclei, any d/dR matrix element that involves a *constant* orbital, centered on the heavy nucleus, will be zero. Such orbitals can then serve to generate diabatic subspaces for excitation processes of the heavy atom and, as well, for charge-transfer reactions. In the latter case, however, one should orthogonalize the atomic orbitals centered on the light nucleus to those centered on the heavy nucleus. With such orthogonal orbitals ϕ_i one has the relation

$$\langle \phi_i | d/dR | \phi_j \rangle = -\langle \phi_j | d/dR | \phi_i \rangle \qquad (3)$$

for all R values. Furthermore orthonormal orbitals allow for the use of simple Slater rules[31] for the evaluation of the d/dR matrix elements between two Slater determinants.

B. Wave functions, potentials, and couplings

The use of atomic orbitals implies an approach based on a valence-bond (VB) description of the states. In the particular $(HKr)^+$ case, the VB state issuing from $H^+ + Kr(4p^6)$ is written only in terms of the orthonormal Kr atomic orbitals,

$$\bar{X}^1\Sigma^+ = |\sigma 1s_{Kr}\bar{\sigma}1s_{Kr}\cdots\bar{\sigma}4p_{Kr}|, \qquad (4)$$

and the $\bar{I}^1\Sigma^+$ state coming from $H + Kr^+(4p^5)$ appears as

$$\bar{I}^1\Sigma^+ = (1/\sqrt{2})\left(|\sigma 1s_{Kr}\bar{\sigma}1s_{Kr}\cdots\sigma 4p_{Kr}\bar{\sigma}1\bar{s}_H| - |\sigma 1s_{Kr}\bar{\sigma}1s_{Kr}\cdots\bar{\sigma}4p_{Kr}\sigma 1\bar{s}_H|\right) \qquad (5)$$

In Eq. (5) $1\bar{s}_H$ is a $1s_H$ atomic orbital from which any component in the Kr ground-state atomic orbitals that may arise as R varies is projected out; i.e.,

$$1\bar{s}_H = \mathfrak{N}(R)\left(1s_H - \sum_i \langle \sigma\phi^i_{Kr} | \sigma 1s_H\rangle \sigma\phi^i_{Kr}\right), \qquad (6)$$

$\mathfrak{N}$ being a normalization factor. Equation (6) de-

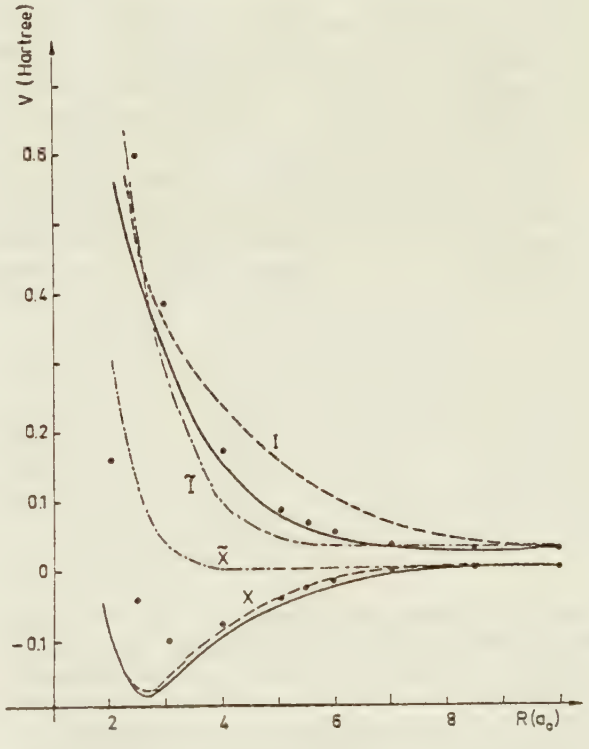


FIG. 2. Potential-energy curves for the two lowest $^1\Sigma^+$ states. – – –: SCF calculations; ——: SCF-CI calculations; –·–·–: PVB calculations; ···: PVB-CI calculations.

fines a projected atomic orbital as suggested by O'Malley.[19] However, contrary to his suggestion, we do not use $\tilde{\phi}_{Kr}$ orbitals that could be defined with an equation equivalent to (6), since such orbitals would still give rise to unwanted d/dR matrix elements. Hence the suggestions of both Smith[18] and O'Malley[19] meet in the present treatment. Furthermore, a VB approach is just the starting point of the charge-transfer model described by Demkov[10]; the problem of nonorthogonal electronic states mentioned by Demkov is avoided here by the use of the procedure described above.

The matrix elements of the electronic hamiltonian H_{el} between the projected VB states (PVB) (or VB states built up from projected atomic orbitals), of, e.g., types (4) and (5), have been calculated by using the ALCHEMY program facilities. The $\langle \tilde{X}^1\Sigma^+ | H_{el} | \tilde{X}^1\Sigma^+ \rangle$ and $\langle \tilde{I}^1\Sigma^+ | H_{el} | \tilde{I}^1\Sigma^+ \rangle$ PVB potential-energy curves shown in Fig. 2 are almost parallel from infinite values of R down to internuclear distances $R \simeq 5a_0$. Since by construction the $\langle \tilde{X} | d/dR | \tilde{I} \rangle$ matrix element is equal to zero (within the assumption that the center of mass of the nuclei coincides with the Kr nucleus), the remaining *direct* coupling between the $\tilde{X}$ and $\tilde{I}$ PVB states is due only to the $\langle \tilde{X} | H_{el} | \tilde{I} \rangle$ matrix element shown in Fig. 3.

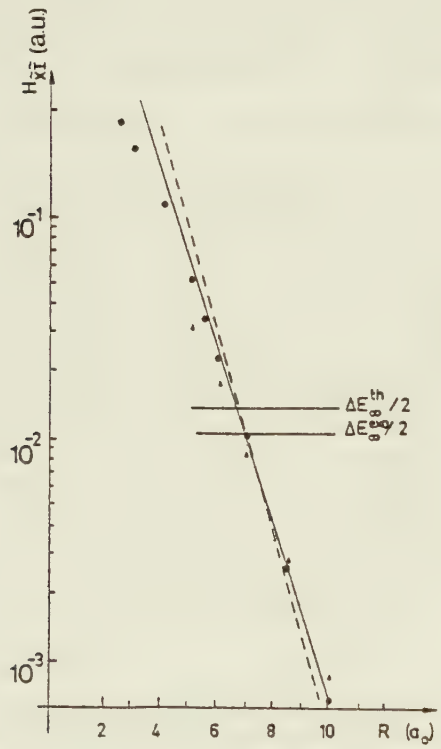


FIG. 3. Comparison of the PVB $\langle \tilde{X}^1\Sigma^+ | H_{el} | \tilde{I}^1\Sigma^+ \rangle$ coupling (•••) with the model charge-exchange interactions predicted by Johnson *et al.* (Ref. 13) (– – –) and Olson *et al.* (Ref. 34) (▲). The solid curve is a purely exponential fit to the present calculated values at large internuclear distances. Half the resonance energy defect of the separated-atom levels is shown as a horizontal line [ΔE^{th}: present theoretical result; ΔE^{expt}: deduced from the data of Moore (Ref. 36)].

Although it would seem that the above procedure is just a mathematical artifact to cancel the d/dR matrix elements, it will be seen, from the following discussions, that the PVB approach yields good results for the potential-energy curves and wave functions at large R, thus enabling a convenient and accurate description of the charge-transfer transition.

C. Charge-exchange interaction

In this section we compare the $\langle \tilde{X} | H_{el} | \tilde{I} \rangle$ interaction with earlier predictions made by a number of authors. This interaction can be fitted to better than 1% (for $R \geq 2.5a_0$) by the analytical function

$$H_{\tilde{X}\tilde{I}} = AR^{\alpha} e^{-\gamma R}, \tag{7}$$

with $A = 1.0194$, $\alpha = 1.542\,56$, and $\gamma = 1.086\,22$ (in atomic units). The parameter γ governing the exponential decrease of the coupling, at large R is close to that predicted by the formula[32, 33]

$$\gamma = \tfrac{1}{2}\left[(2I_H)^{1/2} + (2I_{Kr})^{1/2} \right] = 1.01 a_0^{-1} \tag{8}$$

(I_H and I_{Kr} being the ionization potentials of H and Kr, respectively). Also, the parameter α is given in the theory of Smirnov[32] by

$$\alpha = 2/\gamma - 1 \simeq 1 . \tag{9}$$

This value of α is in disagreement with that obtained from the present calculation [Eq. (7)]. Nevertheless, model interactions such as those assumed by Johnson *et al.*[13] ($A = 1.5$, $\alpha = 0$, $\gamma = 1$) and Olson *et al.*[34] ($A = 0.7$, $\alpha = 1$, $\gamma = 0.86$) agree reasonably well with the present results and yield about the same value of the critical transition region[17] ($R \simeq 7a_0$) (see Fig. 3). Consequently for such a comparison the detailed behavior of the preexponential function does not seem to be essential, provided that it is properly normalized.

D. Comparison with SCF results

Coming back to the indirect interaction via doubly excited states, we find in the PVB treatment that it is two orders of magnitude smaller than that discussed for the SCF states (see Sec. II). Hence its effect should be reduced accordingly, and it can consequently be neglected. CI calculations limited to ten PVB terms show that this is indeed the case. This PVB-CI calculation also shows, in agreement with the predictions of Johnson *et al.*,[13] that the ground-state potential

TABLE IV. Comparison between SCF and PVB results. The first two columns list the energy difference between the two lowest $^1\Sigma^+$ states resulting from limited CI calculations. The last three columns give values obtained for the lowest $^3\Pi$ potential-energy curve (all of the data are in atomic units).

R	ΔE (SCF-CI)	ΔE (PVB-CI)	$E_{^3\Pi}$ SCF	SCF-CI	PVB
1	0.7471	0.9073	−2745.9900		
2	0.7307	0.8135	−2748.8112		
2.5	0.6154	0.6483	−2749.0616		
3	0.4874	0.4842	−2749.1639	−2749.1922	−2749.1822
4	0.2597	0.2555	−2749.2160		−2749.2495
5	0.1238	0.1174	−2749.2319	−2749.2827	−2749.3064
5.5	0.0850	0.0821	−2749.2395		
6	0.0593	0.0588	−2749.2475	−2749.2822	−2749.2785
7	0.0345	0.0354	−2749.2620		−2749.2789
8.5	0.0282	0.0280	−2749.2750		
10	0.0279	0.0277	−2749.2782		

well is largely due to the charge-transfer interaction H_{XI} between the lowest two $^1\Sigma^+$ PVB states (Fig. 2). The discrepancy observed at $R \leq 4a_0$ between the PVB − CI and the ground-state potential well of the $(HKr)^+$ system is mainly attributable to the limited dimension of the CI calculation which cannot balance the lack of polarization of the orbitals involved in the PVB configuration-state-functions. This has actually been verified by carrying out one-center SCF calculations in which we studied the variation with R of the Kr ground-state energy as an H^+ ion is approached. In this calculation only the Kr orbitals given in Table I were involved. Such a constraint prevents the Kr electrons from being shared with the proton. The energy curve obtained in this way represents the amount of distortion of the Kr ground-state orbitals allowed by the STO expansion basis. At relatively small internuclear distances, this polarization energy accounts to a large extent for the energy defect between the SCF-CI and the PVB-CI ground-state potentials. For instance, at $R = 3a_0$ this polarization energy amounts to 0.05 hartree, which represents more than 80% of the 0.06-hartree energy difference between the SCF-CI and the PVB-CI ground states.

Yet the $X - I$ and the $\tilde{X} - \tilde{I}$ energy differences of, respectively, the SCF-CI and PVB-CI calculations closely agree down to $R \simeq 3a_0$ (Table IV). In addition to the above discussion, the deviations arising at smaller internuclear distances may also be caused by the MO pseudocrossings[3] predicted by the diabatic-correlation rules of Barat and Lichten.[7] It is readily seen that for the purpose of calculating charge-transfer transition probabilities by a close-coupling method which involves the adiabatic potential-energy *differences* (Table IV) and the corresponding d/dR couplings (as, e.g., in the impact-parameter method) both the SCF-CI and PVB-CI treatments will yield the same answer. The d/dR matrix element in the PVB-CI adiabatic basis, $(\tilde{X}^{ad}, \tilde{I}^{ad})$, is easily obtained with the formula[35]

$$\langle \tilde{X}^{ad} | d/dR | \tilde{I}^{ad} \rangle = \left(\frac{\Delta dH_{XI}}{dR} - H_{XI} \frac{d\Delta}{dR} \right) \Big/ (\Delta^2 + 4H_{XI}^2), \tag{10}$$

where Δ is the energy difference between the diabatic $\tilde{X}^1\Sigma^+$ and $\tilde{I}^1\Sigma^+$ PVB states. This matrix element is shown in Fig. 4. In the same figure are shown the corresponding d/dR matrix elements obtained at $6a_0$ and $7a_0$ in the SCF-CI approach. The close agreement between the SCF-CI and the PVB-CI data points yields further confidence in the quality of the equivalent diabatic PVB representation.

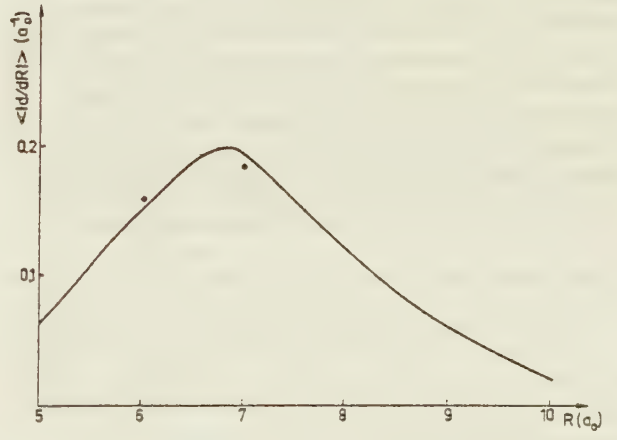


FIG. 4. d/dR matrix element between the two lowest $^1\Sigma^+$ states of the $(Kr\text{-}H)^+$ system: —— : PVB-CI results; ●: SCF-CI results.

From Table IV it appears that the $^3\Pi$ state, obtained in the virtual-orbital approximation from the $X^1\Sigma^+$-SCF molecular orbitals, is more affected by CI than is the $^3\Pi_{PVB}$ state. The latter state is thus closer to the $^3\Pi$-SCF state, which provides (within a given basis set) the best variational $^3\Pi$ wave function corresponding to a single molecular configuration. This indicates that the charge-transfer interaction mostly affects the orbitals of the lowest Σ^+ states, whereas those of the $^3\Pi$ state remain almost atomic orbitals down to relatively small internuclear distances. The same would also hold true for the $^1\Pi$ state.

The definition equivalent to Eq. (5) for the $^1\Pi_{PVB}$ state, e.g.,

$$^1\Pi_{PVB} = (1/\sqrt{2})(|\ldots\sigma 4p_{Kr}\bar{\sigma}4p_{Kr}\sigma 1s_H\ldots\bar{\pi}^+4p_{Kr}\bar{\pi}^-4p_{Kr}| - |\ldots\sigma 4p_{Kr}\bar{\sigma}4p_{Kr}\sigma 1s_H\ldots\bar{\pi}^+4p_{Kr}\pi 4p_{Kr}|), \tag{11}$$

shows that there exists no direct rotational coupling between the $\tilde{X}^1\Sigma^+$ and $^1\Pi_{PVB}$ states, since the matrix element $\langle 1s_H|L^+|\pi^-4p_{Kr}\rangle$ vanishes from Eq. (6). In the same way, the direct $\tilde{X}^1\Sigma^+$-$^3\Pi_{PVB}$ spin-orbit interaction is zero. Hence it appears that in the PVB basis set the $H_{\tilde{X}\tilde{I}}$ matrix element causes primarily the population of the $\tilde{I}^1\Sigma^+$ charge-transfer channel, which in turn feeds the other channels ($^{3,1}\Pi_{PVB}$). The matrix elements that cause this population sharing are readily seen to be just the atomic matrix elements $\langle\sigma 4p_{Kr}|L^+|\pi^+4p_{Kr}\rangle = \sqrt{2}$ and $\langle\tilde{I}^1\Sigma^+_{(\Omega=0)}|H_{SO}|^3\Pi_{PVB(\Omega=0)}\rangle = 0.0115$ hartree.[36]

IV. DIABATIC STATES FOR SPIN-ORBIT COUPLING

Although according to the discussion of Sec. I the spin-orbit interaction contributes negligibly to the primary direct transition from the incoming state ($H^+ + Kr \to X^1\Sigma^+$), it participates in the population sharing between the $H + Kr^+(^2P_{3/2})$ and $H + Kr^+(^2P_{1/2})$ channels. How can such a process occur in the adiabatic basis set of $\Omega = 0^+$ states that diagonalize the $H_{el} + H_{SO}$ operator? This may be seen by noting that the diagonalization procedure is achieved with an R varying linear combination of the $I^1\Sigma^+_{(\Omega=0^+)}$ and the $^3\Pi_{(\Omega=0^+)}$ states,

$$|\phi_1\rangle = c(R)|I^1\Sigma^+\rangle + s(R)|^3\Pi\rangle,$$
$$|\phi_2\rangle = -s(R)|I^1\Sigma^+\rangle + c(R)|^3\Pi\rangle. \tag{12}$$

Hence the adiabatic states for the spin-orbit interaction satisfying $\langle\phi_1|H_{el}+H_{SO}|\phi_2\rangle = 0$ are still coupled by the radial (dynamical) operator $v_R d/dR$,

$$\langle\phi_1|d/dR|\phi_2\rangle = -c^{-1}\frac{ds}{dR}. \tag{13}$$

This relation is obtained by noting that the $I^1\Sigma^+$ and the $^3\Pi$ states are in a sense diabatic with respect to each other,[18] since $\langle{}^1\Sigma^+|d/dR|^3\Pi\rangle = 0$ for symmetry reasons. Instead of dealing with the adiabatic states $|\phi_1\rangle$ and $|\phi_2\rangle$ and their d/dR coupling, one may alternatively use the $|I^1\Sigma^+\rangle$ and $|^3\Pi\rangle$ diabatic states coupled by the $\langle I^1\Sigma^+|H_{SO}|^3\Pi\rangle$ matrix element. A drawback of the latter approach is that the $I^1\Sigma^+$ and $^3\Pi$ states still interact at $R \to \infty$, which prevents us from recovering the proper assymptotic conditions that allow for extracting the scattering matrix. Yet it is still possible, at sufficiently large R, to perform a suitable basis change that transforms the molecular states ($^1\Sigma^+$, $^3\Pi$) into the actual proper spin states of the separated atoms. Such a treatment is analogous to that suggested by Stern *et al.*[20] for solving the troubles caused by the incorrect dissociation of LCAO single-configuration states in homonuclear systems.

However, since any *constant linear combination* of the $I^1\Sigma^+$ and $^3\Pi$ states still gives rise to a zero matrix element of the d/dR operator, one may equally well choose another twofold diabatic subspace, namely, that which diagonalizes the $H_{el}+H_{SO}$ operator at $R \to \infty$. The two states of such a basis, i.e.,

$$|\Gamma_1\rangle = (-\sqrt{2}\,|I^1\Sigma^+\rangle + |^3\Pi\rangle)/\sqrt{3},$$
$$|\Gamma_2\rangle = (|I^1\Sigma^+\rangle + \sqrt{2}\,|^3\Pi\rangle)/\sqrt{3}, \tag{14}$$

interact through the matrix element $\langle\Gamma_1|H_{el}+H_{SO}|\Gamma_2\rangle$, which is proportional[37] to the energy difference between the $I^1\Sigma^+$ and $^3\Pi$ states.[38] The latter matrix element may become very large as R decreases below $6a_0$. However, this does not matter for the present purpose of studying the population sharing caused by the spin-orbit interaction during collision. Still, for physical significance it is always possible to perform a trivial basis charge to the weakly interacting $I^1\Sigma^+$ and $^3\Pi$ states at internuclear distances far enough below the critical region where the electronic transitions take place. Hence either pair of diabatic states, (Γ_1, Γ_2) or ($I^1\Sigma^+$, $^3\Pi$), may serve to handle the population sharing between the two $\Omega = 0^+$ states dissociating into $H + Kr^+(4p^5\,{}^2P_{1/2}, {}^2P_{3/2})$ and a transformation from one basis to the other may be performed when actually needed.

V. CONCLUSIONS

The methods presented in this paper for handling the $(H\text{-}Kr)^+$ system proceed from two points of view which actually date from the early days of quantum mechanics. One approach is based on LCAO-SCF adiabatic molecular orbitals, which are found to properly describe the system at rela-

tively small R; the second method is based on essentially atomic, almost frozen, orbitals, which simply allow for the treatment of the charge-transfer transitions at large R. Also, the two diabatic procedures discussed for treating the spin-orbit interaction proceed from the same points of view. One procedure involves the almost-good atomic quantum numbers related to the dominant spin-orbit effects at large R, whereas the other procedure involves the good quantum numbers related to the dominant molecular axial field set up by the two-center electrostatic interactions. It appears here that the change induced in the passage from one region of interaction to the other (atomic $\rightleftharpoons$ molecular) is actually the source of the nonadiabatic transitions, as illustrated by the behavior of the d/dR matrix elements in the adiabatic basis.

The small number of close-lying and well-isolated states investigated here participate in the primary excitation mechanism through which all of the other excited channels are reached.[8] The study of the other excitation processes will require methods for handling the inner MO crossings at $R \simeq 2.5a_0$ as well as a much larger number of states. Also, the theoretical analysis of the double charge-transfer processes[39] should take into account the type of transition discussed in Sec. II.

ACKNOWLEDGMENTS

We are indebted to Dr. J. Durup, Dr. M. Barat, and Dr. J. P. Gauyacq for helpful discussions, and to Dr. J. P. Gauyacq for communicating his d/dR program.

---

*Present address: Laboratoire des Collisions Atomiques, Bât. 220, Université Paris-Sud, 91405 Orsay, France.

[1]R. L. Champion, L. D. Doverspike, W. G. Rich, and S. M. Bobbio, Phys. Rev. A 2, 2327 (1970).
[2]H. P. Weise, H. V. Mittman, A. Ding, and A. Henglein, Z. Naturforsch. A 26, 1112 (1971).
[3]T. F. Moran and L. Friedman, J. Chem. Phys. 40, 860 (1964).
[4]H. F. Helbig and W. E. Ferguson, Phys. Rev. A 6, 519 (1972).
[5]W. G. Rich, S. M. Bobbio, R. L. Champion, and L. D. Doverspike, Phys. Rev. A 4, 2253 (1971).
[6]H. H. Fleischman and R. A. Young, Phys. Rev. Lett. 19, 941 (1967).
[7]M. Barat and W. Lichten, Phys. Rev. A 6, 211 (1972).
[8]M. Abignoli, J. Baudon, M. Barat, J. Fayeton, and J. C. Houver, J. Phys. B 5, 1633 (1972).
[9]D. S. F. Crothers, J. Phys. B 6, 1418 (1973), and references therein.
[10]Y. N. Demkov, Zh. Eksp. Teor. Fiz. 45, 195 (1963) [Sov. Phys.–JETP 18, 138 (1964)].
[11]See, e.g., M. Barat, J. C. Brenot, D. Dhuicq, J. Pommier, V. Sidis, R. E. Olson, E. J. Shipsey, and J. C. Browne, J. Phys. B 9, 269 (1976), for an example of an oscillating pattern created by a Demkov-type transition.
[12]D. W. Koopman, Phys. Rev. 154, 79 (1967).
[13]R. E. Johnson, C. E. Carlson, and J. W. Boring, Chem. Phys. Lett. 16, 119 (1972).
[14]R. Shakeshaft and J. Macek, Phys. Rev. A 7, 1554 (1973).
[15]Examples of d/dR radial coupling matrix elements for large CI wave functions of the $(H\text{-}He)^+$ system are presented in the paper of T. A. Green, H. H. Michels, J. C. Browne, and M. M. Madsen, J. Chem. Phys. 61, 5186 (1974).
[16]Examples of d/dR radial coupling matrix elements for SCF wave functions can be found, e.g., in J. S. Briggs and K. Taulbjerg, J. Phys. B 8, 1909 (1975), and V. Sidis, N. Stolterfoht, and M. Barat, in Abstracts of the Papers of the Second International Conference on Inner Shell Ionization Phenomena, Freiburg, 1976, p. 68.
[17]E. C. G. Stueckelberg, Helv. Phys. Acta 5, 369 (1932).
[18]F. T. Smith, Phys. Rev. 179, A111 (1969).
[19]T. F. O'Malley, J. Chem. Phys. 51, 322 (1969).
[20]B. Stern, J. P. Gauyacq, and V. Sidis (unpublished); also in *Electronic and Atomic Collisions, Abstracts of the Papers of the Ninth International Conference on the Physics of Electronic and Atomic Collisions*, edited by J. S. Risley and R. Geballe (Univ. of Washington, Press, Seattle, 1975), Vol. 2, p. 603.
[21]C. Benoit, C. Kubach, V. Sidis, J. Pommier, and M. Barat, in Ref. 20, Vol. 1, p. 169, and unpublished.
[22]P. S. Bagus, B. Liu, A. D. Mc Lean, and M. Yoshimine (unpublished). Preliminary descriptions of the ALCHEMY program are given by A. D. McLean, in *Proceedings of the Conference on Potential Energy Surfaces in Chemistry* (California U.P., Santa Cruz, 1970), and by P. S. Bagus, in *Selected Topics in Molecular Physics*. (Verlag Chemie, Berlin, 1972). See also IBM Research Publication No. 14748 (1971) (unpublished).
[23]E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2686 (1963).
[24]E. Clementi, J. Chem. Phys. 41, 303 (1964).
[25]S. Peyerimhoff, J. Chem. Phys. 43, 998 (1965).
[26]C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
[27]C. Kubach and V. Sidis, J. Phys. B 6, L289 (1973).
[28]R. Daudel, R. Lefebvre, and C. Moser, *Quantum Chemistry* (Interscience, New York, 1959), p. 475.
[29]C. Kubach, Ph.D. thesis (Université de Paris VI, 1974) (unpublished).
[30]V. Sidis, in *The Physics of Electronic and Atomic Collisions, Invited Lectures and Progress Reports of the Ninth International Conference on the Physics of Electronic and Atomic Collisions*, edited by J. S. Risley and R. Geballe (Univ. of Washington Press, Seattle, 1975), p. 295.
[31]J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 1.
[32]B. M. Smirnov, Zh. Eksp. Teor. Fiz. 47, 518 (1964) [Sov. Phys.–JETP 20, 345 (1965)]; B. M. Smirnov,

Atomic Collisions and Elementary Processes in Plasma (Atomizdat, Moscow, 1968).
[33]E. L. Duman, in *Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, 1971, Abstracts of Papers*, edited by L. M. Branscomb *et al.* (North-Holland, Amsterdam, 1971), p. 471.
[34]R. E. Olson, F. T. Smith, and E. Bauer, Appl. Opt. 10, 1848 (1971).
[35]R. D. Levine, B. R. Johnson, and R. B. Bernstein, J. Chem. Phys. 50, 1694 (1969).
[36]C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, D.C., 1952).
[37]It is assumed that the H_{ee} matrix element is independent of R. This is indeed the case in the PVB basis set (see Sec. III D).
[38]F. M. Mies, Phys. Rev. A 7, 942 (1973).
[39]J. Appell, Ph.D. thesis (Université de Paris XI, 1972) (unpublished).

DISCUSSION ET COMMENTAIRES

1 - Le fait que le potentiel d'ionisation de Kr soit supérieur à celui de H nous permet, lors des calculs LCAO-SCF, de décrire l'état I corrélé à Kr^+ ($4p^5$) + H, à l'aide des orbitales occupées et virtuelles de l'état X. On évite ainsi les optimisations séparées des états X et I et les problèmes rencontrés pour le système H^+ + Xe (cf chapitre IV).

2 - Le sous-espace sous-tendu par les états PVB : $\tilde{X}\,{}^1\Sigma^+$ et $\tilde{I}\,{}^1\Sigma^+$ n'est rigoureusement diabatique, au sens de Smith /36/, que si l'on considère que le centre de masse des noyaux est sur le noyau de Kr. Pour tester la valeur de cette approximation, nous avons calculé le couplage radial entre les états $\tilde{X}$ et $\tilde{I}$ qui s'écrit comme :

$$\langle \tilde{I} \,|\, \partial/\partial R \,|\, \tilde{X} \rangle = \sqrt{2}\ \langle 1\tilde{s}_H \,|\, \partial/\partial R \,|\, 4p_{Kr} \rangle$$

Cette dernière expression est aisément calculable puisqu'elle met en jeu une orbitale constante : $4p_{Kr}$. En effet, le calcul de la dérivée des coefficients du développement des orbitales moléculaires sur la base des orbitales atomiques (cf chapitre II) est ainsi évité.
Nous avons obtenu :

$$\langle \tilde{I} \,|\, \partial/\partial R \,|\, \tilde{X} \rangle = 0{,}001\ a_o^{-1} \quad \text{et} \quad 0{,}0001\ a_o^{-1}$$

respectivement pour R = 6 et 7 a_o. Ces valeurs sont tout-à-fait négligeables devant les couplages radiaux résultant de l'intéraction des configurations dans la base PVB (cf fig. 4). Elles sont même pratiquement de l'ordre de grandeur des erreurs numériques introduites par le programme calculant les éléments de la matrice $\partial/\partial R$ entre orbitales moléculaires. L'importance de ces erreurs dépend essentiellement du nombre des orbitales de Slater de base et de la précision des développements des orbitales moléculaires sur la base des orbitales de Slater. Pour estimer cette erreur, on calcule :

$$\langle \phi_a \mid \partial/\partial R \mid \phi_a \rangle$$

où ϕ_a désigne une orbitale réelle normalisée. On doit vérifier :

$$\langle \phi_a \mid \partial/\partial R \mid \phi_a \rangle = 0$$

(On obtient cette relation en dérivant, par rapport à R, la norme constante de ϕ_a).

En calculant cette expression pour l'orbitale 8σ, résultat du calcul SCF, nous avons obtenu à $R = 7\ a_o$:

$$\langle 8\sigma \mid \partial/\partial R \mid 8\sigma \rangle = 0{,}00006\ a_o^{-1}$$

3 - Les transitions responsables de l'échange de charge s'effectuent principalement autour d'une distance R_c définie par la relation /22/ :

$$H_{12}(R_c) = \frac{1}{2}\Delta E$$

La distance R_c correspond au maximum du couplage radial dans la base adiabatique correspondante, si :

a) la séparation énergétique entre les deux courbes de potentiel est rigoureusement constante,

b) le couplage H_{12} est rigoureusement exponentiel.

En effet, en dérivant la relation (10) par rapport à R, on obtient un couplage radial maximum, quand la relation :

$$\frac{d^2 H_{12}}{dR^2}\ (\Delta^2 + 4\ H_{12}^2) = 8\ H_{12}\left(\frac{dH_{12}}{dR}\right)^2$$

est vérifiée, ce qui donne avec $H_{12} = Ae^{-\lambda R}$

$$H_{12}(R_c) = \frac{1}{2}\Delta E$$

4 - Double transfert de charge

On peut se demander si, d'une façon générale, le double transfert de charge :

$$H^+ + Kr \rightarrow H^- + Kr^{++}$$

se fait directement ou par l'intermédiaire des voies correspondant au simple échange de charge.

Pour répondre à cette question, nous avons examiné le rapport des intéractions $H_{\tilde{X}\tilde{I}}$, $H_{\tilde{X}\tilde{D}}$ et $H_{\tilde{I}\tilde{D}}$ aux séparations énergétiques correspondantes ($E_{\tilde{I}}-E_{\tilde{X}}$, $E_{\tilde{D}}-E_{\tilde{X}}$, $E_{\tilde{D}}-E_{\tilde{I}}$) dans la base formée par les trois états diabatiques $\tilde{X}^1\Sigma^+$, $\tilde{I}^1\Sigma^+$, $\tilde{D}^1\Sigma^+$ * résultant du calcul PVB. Le rapport : $H_{\tilde{X}\tilde{D}} / (E_{\tilde{X}}-E_{\tilde{D}})$ reste extrêmement petit (inférieur à 0,03) pour toute valeur de R, par contre, le rapport $\frac{H_{\tilde{I}\tilde{D}}}{E_{\tilde{D}}-E_{\tilde{I}}}$ atteint la valeur 0,1 autour de $R = 4\ a_o$. On en conclut donc que la population de l'état $\tilde{D}^1\Sigma^+$, c'est-à-dire l'obtention de Kr^{++} dans les états $^1S_0$ et $^1D_2$ ne se fait pas par une transition directe X→D mais en deux étapes: une première transition X→I (localisée autour de $R_c = 7\ a_o$), suivie de la transition I→D dont la localisation est plus délicate. Toutefois la faiblesse du rapport $H_{\tilde{I}\tilde{D}} / (E_{\tilde{D}}-E_{\tilde{I}})$ fait que cette seconde transition doit être de faible amplitude. Notons enfin que le calcul complet des sections efficaces de double transfert de charge présente la difficulté de requérir une base de grande dimension (cf chapitre VI) et pose le problème d'une description correcte de l'état électronique de H^-.

---

* L'état $D^1\Sigma^+$ de configuration $1s_{Kr}$..... $1\tilde{s}^2_H$ est corrélé à R ∞ à $H^- + Kr^{++}$ $(\sqrt{2}\ ^1D + {}^1S)/\sqrt{3})$ et correspond à l'état diexcité "relais" du calcul LCAO-SCF (cf paragraphe II).

Chapitre VIII

CHARGE EXCHANGE PROCESSES IN PROTON ON RARE GAS COLLISIONS

II H^+ + Kr and lighter systems*

C. Benoit and C. Kubach

Laboratoire des Collisions Ioniques•, Bâtiment 420, Université de Paris-Sud, 91405, Orsay,France.

V. Sidis••, J. Pommier and M. Barat

Laboratoire des Collisions Atomiques•, Bâtiment 220, Université de Paris-Sud, 91405, Orsay,France.

ABSTRACT

Differential measurements on charge transfer processes in H^+ + Kr, Ar collisions have been performed using a time-of-flight technique. Oscillating cross sections for the well resolved $H + Kr^+ (4p^5\ ^2P_{1/2})$ and $H + Kr^+ (4p^5\ ^2P_{3/2})$ processes are observed in the angular ($0.2 \text{ deg} \leqslant \theta \leqslant 3 \text{ deg}$) and energy ($100 \text{ eV} \leqslant E \leqslant 350 \text{ eV}$) ranges covered by experiments. A theoretical investigation of the near resonant charge transfer processes, based on a previous molecular study of the H^+-Kr collisional system, is presented. The calculations involving the diabatic " projected valence-bond " basis are found to satisfactorily agree with experiment. The picture used for handling the H^+ + Kr collision is further extented to the lighter systems. In particular, total cross sections for near resonant charge transfer in the H^+ - Ar, Ne, He systems are calculated using a simple procedure (Olson 1972) and found to agree at low energy ($E \lesssim 10$ keV) with previous experimental data.

• Associated with the C.N.R.S.

•• CMOA, 23 rue du Maroc, 75019 Paris,France.

---

* Soumis pour publication à J. Phys. B

1. INTRODUCTION

Previous measurements (Stedeford and Hasted 1955, Stier and Barnett 1956, Williams and Dunbar 1966, De Heer et al. 1966, Koopman 1967, Becker and Scharmann 1969) revealed that total cross sections for charge transfer in the H^+ - Xe, Kr, Ar systems could reach several $Å^2$ at moderate collision energies. In contrast, much smaller cross sections were obtained at all energies in the lighter systems: H^+ - Ne, He. The importance of charge transfer in the H^+ - rare gas (RG) systems was soon related to the magnitude of the resonance energy defect between the $H^+ + RG(np^6)$ and the $H(1s) + RG^+(np^5)$ channels (Rapp and Francis 1962). This was noticed by Abignoli et al. (1972) who, in addition, emphasized the major primary role of this " near resonant " charge transfer process in the production mechanism of other inelastic processes of the type : $H^+ + RG^*$ and $H^* + RG^+$. Structure was also found in the total differential cross sections (i. e. the sum of all differential cross sections) for charge transfer. This feature was tentatively attributed to interferences created when the system travels accross a critical transition region located at large internuclear distances (Fleischmann and Young 1967, Abignoli et al. 1972). The contribution of a rainbow phenomenon to this structure was also recognized by Fleischmann and Young (1967).

In the first paper of this series (Kubach et al. 1976), here after refered to as I), devoted to the $H^+ + Xe$ collision, the features observed in the charge transfer cross sections were understood by refering to curve-crossing effects. In contrast, no such crossing is expected, from the Barat - Lichten (1972) correlation rules, in the lighter H^+ - RG systems (Abignoli et al. 1972). Yet, from the near resonant charge transfer theory (Stueckelberg 1932, Rosen and Zener 1932, Bates 1962, Demkov 1964, Nikitin 1968, 1969, 1971, Olson 1972, Crothers 1971, 1973), one still expects a localized transition region around the critical internuclear distance (R_c), where the coupling (H_{12}) between the $H^+ + RG$ and the $H + RG^+$ channels is of the order of half the resonance energy defect (ΔE). The interpretation of the oscillations

in the near resonant charge transfer cross sections as due to both rainbow and "Stueckelberg - Demkov " interferences then proceeds along the same semi-classical ideas as developed in I.

The study initiated in I is extended here to the H^+ + Kr, Ar systems. For H^+ - Kr, the large spin orbit splitting (Kr^+ $4p^5$ $^2P_{1/2}$, $^2P_{3/2}$) still allows for the measurement of individual cross sections, whereas for H^+ - Ar the corresponding sublevels could not be resolved. Electron capture into higher excited states are also identified and the corresponding cross sections are reported for both systems.

The theoretical investigation is based on the molecular approaches proposed by Kubach and Sidis (1976). These results are involved in quantal close coupling calculations of the elastic and near resonant charge transfer cross sections for the H^+ + Kr system. Of the two procedures suggested in that paper, the " projected-valence-bond " (PVB) treatment, which fits with the general lines of the Demkov model (1964), agrees best with experiment. This prompted us to extend the same ideas to the study of charge transfer in the lighter H^+ - Ar, Ne, He systems. Total charge transfer cross sections are then calculated using a simple procedure based on the reduced universal cross sections reported by Olson (1972).

2.EXPERIMENTS

The various charge transfer processes are identified by the energy loss undergone by the scattered neutral H atoms. The energy losses ΔE are determined using a T.O.F. technique previously described (Brenot et al.1975) and already used in I. A typical angular resolution of 0.2 deg and an energy resolution of 0.4 eV are achieved at a beam energy E = 300 eV. However, the experimental cross sections suffer from large systematic uncertainties at small angles : $\theta \leqslant 0.4$ deg due to the difficulty of accurately estimating the apparatus function near zero degrees (see I).

2.1. Energy loss spectra

2.1.1. H^+ + Kr

Typical energy loss spectra are shown in Fig. 1 and 2. The well resolved peaks A and B[(*)] (fig. 1) are attributed to the reactions :

A. $H^+ + Kr\ (4p^6) \longrightarrow H(n=1) + Kr^+\ (4p^5\ ^2P_{3/2}), \quad \Delta E = 0.4$ eV

B. $H^+ + Kr\ (4p^6) \longrightarrow H(n=1) + Kr^+\ (4p^5\ ^2P_{1/2}), \quad \Delta E = 1.06$ eV

At larger reduced angles ($\tau = E\theta$) excitation of H and Kr^+ is also observed (Fig. 2). The peak C can be ascribed without ambiguity to :

$$H^+ + Kr\ (4p^6) \longrightarrow H(n=2) + Kr^+\ (4p^5\ ^2P_{3/2,\ 1/2}), \quad 10.6 \leqslant \Delta E \leqslant 11.3 \text{ eV}$$

On the other hand three processes can account for peak D namely :

$$H^+ + Kr\ (4p^6) \longrightarrow \begin{cases} H\ (n=3) + Kr^+\ (4p^5\ ^2P_{3/2,\ 1/2}) & 12.5 \leqslant \Delta E \leqslant 13.2 \text{ eV} \\ H\ (n=1) + Kr^{+*}(4s4p^6\ ^2S_{1/2}) & \Delta E = 13.90 \text{ eV} \\ H\ (n=4) + Kr^+\ (4p^5\ ^2P_{3/2,\ 1/2}) & 13.2 \leqslant \Delta E \leqslant 13.9 \text{ eV} \end{cases}$$

These processes cannot be resolved within our energy resolution for $E \geqslant 350$ eV.

2.1.2. H^+ + Ar

A typical energy loss spectrum of H atoms scattered from the H^+ + Ar collision , at E = 520 eV, is shown in Fig. 3. For this system the smallness of the spin orbit splitting ($\Delta E = 0.2$ eV) prevents from the

---

Footnote : (*) The labeling A and B has erroneously been interchanged in the paper of Benoit et al. (1975).

separation of the Ar^+ ($3p^5\ ^2P_{1/2\ ,\ 3/2}$) sublevels. Peak A, B corresponds to near resonant charge transfer :

$$H^+ + Ar\ (3p^6) \longrightarrow H(n=1) + Ar^+\ (3p^5\ ^2P) \qquad \Delta E = 2.19\ eV$$

Peaks C and D correspond to charge transfer involving excitation of either H or Ar according to the reactions :

$$C.\quad H^+ + Ar\ (3p^6) \longrightarrow H(n=2) + Ar^+\ (3p^5\ ^2P) \qquad \Delta E = 12.39\ eV$$

$$D.\quad H^+ + Ar(3p^6) \longrightarrow \begin{cases} H(n=3) + Ar^+\ (3p^5\ ^2P) & \Delta E = 14.94\ eV \\ H(n=4) + Ar^+\ (3p^5\ ^2P) & \Delta E = 14.24\ eV \\ H(n=1) + Ar^{+*}(3s\ 3p^6\ ^2S) & \Delta E, = 15.69\ eV \end{cases}$$

2.2. Differential cross sections

2.2.1. H^+ + Kr

Reduced differential cross sections for processes A and B (ρ_A and ρ_B respectively) are presented in Fig. 4. The relative importance of processes A and B remains about of the same order of magnitude for all the investigated energies (Fig. 5). This is in contrast with the behaviour observed in the H^+ + Xe collision for the ratio of the A and B processes in the range 100 eV$\lesssim$E$\leqslant$330 eV. It is not clear whether this trend extends to higher energies since above E = 400 eV the energy resolution did not allow for resolving the splitting between the A and B peaks (ΔE = 0.7 eV).

Structure similar to that found in total differential cross sections by Fleischmann and Young (1967) is seen in both the ρ_A and ρ_B cross sections. Figure 4 shows the comparison (at E = 100 eV and 200 eV) between the sum $\rho_A + \rho_B$ and the data of Fleischmann and Young.

Differential cross sections for charge transfer excitation into higher lying levels (processes C and D) are shown along with the $\rho_{A,B}$ cross section in Fig. 6. The ρ_C and ρ_D cross sections start to rise at a much smaller reduced angle ($\tau \simeq 200$ eV.deg) than that of the fall-off in the ρ_A, ρ_B cross sections. Such a feature has also been observed in the H^+ + Xe system and can be explained in the same way.

2.2.2. H^+ + Ar

The reduced differential cross sections at E = 520 eV, shown in Fig. 7 display structures similar to those observed in the H^+ + Kr case . The total differential charge transfer cross section measured by Abignoli et al. (1972) at E = 500 eV is also shown in Fig 7 . Since at small τ values charge transfer excitation (processes C and D) is negligible, the data of Abignoli et al. where brought into coincidence with the present results at $\tau \lesssim 400$ eV deg. The good agreement obtained at larger τ by summing the $\rho_{A,B}$, ρ_C and ρ_D cross sections confirms these previous measurements.

3. THEORY

3.1. Basic molecular approach

As preciously predicted (Koopman 1967, Abignoli et al. 1972 , Shakeshaft and Macek 1973), charge exchange into H + Kr^+ ($4p^5\ ^2P_{3/2}$, $^2P_{1/2}$) levels lying 0.4 eV and 1.06 eV above the ground state H^+ + Kr ($4P^6\ ^1S$) level, is expected to induce the dominant inelastic processes at low and moderate energies. From the molecular analysis of Kubach and Sidis (1976), it appears that among the manifold of states that correlate with H + Kr^+ ($4p^5\ ^2P$), only the $I\ ^1\Sigma^+$ state (Fig. 8) is significantly coupled to the $X\ ^1\Sigma^+$ entrance channel. Two procedures based on different molecular representations have been suggested (Kubach and Sidis 1976) to handle both the perturbed elastic scattering and the above charge transfer processes.

a. Proceeding in a similar manner to that developed in I, the $(H - Kr)^+$ system is treated within the molecular single configuration LCAO - MO - SCF * framework. It was shown by Kubach and Sidis (1976) that, since the Brillouin theorem holds, the X and I states interact either directly via a weak d/dR radial coupling or indirectly via their " potential coupling " (H_{el}) with a doubly excited relay state $D^1\Sigma^+$ (Fig. 8).

Footnote : * Linear Combination of atomic orbitals - Molecular orbitals - Self consistent field.

b. Refering to the Demkov (1964) analysis of the charge transfer mechanism one looks for an essentially atomic representation, of the valence - bond (VB) type, adapted to the description of the system at large internuclear distance (R). In this picture, the assumed diabatic (as defined by Smith 1969) incident and charge transfer channels have nearly parallel energy curves and interact via an exponentially decreasing " potential coupling " . The transition between the two states then preferentially occurs around the distance R_c where the interaction H_{12} becomes of the same order of magnitude as half the resonance energy defect ΔE (Stueckelberg 1932). It was shown by Kubach and Sidis (1976) that the above diabatic atomic representation could actually be achieved by using single configuration valence bond wavefunctions involving projected atomic orbitals (O'Malley 1969). This method has been termed "projected valence bond" (PVB). The incident and charge transfer PVB states, $\tilde{X}\,^1\Sigma^+$ and $\tilde{I}\,^1\Sigma^+$ respectively (Fig. 8), are found to exclusively interact via an exponetially decreasing coupling yielding a critical transition region around $R_c = 7\ a_o$, as predicted by Johnson et al (1972). Although the PVB states lend themselves to a satisfactory and convenient treatment of the charge transfer transition, they fail at small R to fully account for molecular distortion and polarization (Kubach and Sidis 1976). Such a discrepancy is expected to have minor consequences in the calculation of total charge transfer cross sections whereas it should give rise to serious defects in the description of the interference patterns in differential cross sections (especially rainbow structure, Kubach and Sidis 1976). Since in addition at small internuclear distance ($R < R_c$) H_{12} gets much larger than ΔE the atomic description no longer represents physically meaningful states and one should switch to a better suited adiabatic molecular representation based on configuration interaction wave functions (CI). In consequence a basis change, at a distance $R_D < R_c$, from the atomic PVB representation to the molecular SCF - CI representation is required (fig. 8). In pratice this basis change is carried out during the integration of the relevant quantal close coupled equations of the problem. The Gordon (1969, 1971) program, as modified by Stern et al. (1976) enables such a procedure to be actually performed. The determination of R_D is achevied by requiring the results to be stable

against any reasonable arbitrary choice of that distance. Stable results were only obtained for $R_D \leqslant 6a_o$ and the value $R_D = 4a_o$ was actually chosen in the calculations. The upper bound on R_D hence provides an estimate of the width of the transition region ($\sim 1a_o$) around R_c.

In the following, procedure (b), including the basis change at $R_D = 4\ a_o$, will be termed PVB. Results of procedure (a) neglecting the weak $d/_{dR}$ coupling, and called LCAO - SCF throughout, will be presented for comparison.

In order to take the spin-orbit interaction (H_{so}) into account diabatic states for spin-orbit coupling have been used (Kubach and Sidis 1976) in both procedures. These states are expressed as constant linear combinations of the $^3\Pi$ and $^1\Sigma^+$ states (correlated with $Kr^+\ ^2P + H$) thatdiagonalize the H_{so} coupling at $R \to \infty$. Neglecting secondary rotational transitions (see I and Kubach and Sidis 1976) one need only consider the $\Omega = 0^+$ states for treating the elastic and the main inelastic processes of the $H^+ + Kr$ collision.

3.2. Elastic scattering at low energy (E < 20 eV)

From the Massey criterion ($a\,\Delta E \simeq v_M$, where $a = 7\ a_o$ and $\Delta E = 0.4$ eV) it is expected that, for velocities much smaller than $v_M = 0.1$ a.u. (E = 270 eV), the collisional system will behave adiabatically. In such cases, one can simply consider a one - state approximation involving the adiabatic $X^1\Sigma^+$ ($\Omega = 0^+$) molecular ground state issuing from the ground state atomic species : $H^+ + Kr\ (4p^6\ ^1S_o)$. Cross sections for the purely elastic scattering can consequently be derived within this approximation. The corresponding semi-quantal JWKB cross sections (see e.g. Sidis 1972) at E = 6 eV and 15.6 eV (center of mass energy) are shown in Fig 9 a and 9 b. Good agreement is found with the experimental cross sections of Champion et al (1970) at E = 6 eV whereas at E = 15.6 eV the theoretical result displays a small phase shift with

respect to the data of Weise et al. (1971). As a plausible explanation of such a discrepancy, one can invoke the breakdown of the one - state approximation caused, as energy increases, by non - adiabatic coupling to closely lying channels (see Sec 3.1.). However, taking the couplings beetween the three lowest $\Omega = 0^+$ states into account, the PVB calculation at E = 15.6 eV (Fig.9b), shows no appreciable modification of the purely elastic rainbow feature although significant charge transfer occurs at such a low energy (Fig. 9 b). This result shows first that the single average trajectory model of Johnson et al (1972) is unrealistic, as already found by these authors. It is also seen that consideration of the most important inelastic effects, at this low energy, does not improve the agreement with the data of Weise et al (1971). Although many other channels of the type : $H^*(n1) + Kr^+(4p^5)$, $H(1s) + Kr^{+*}(4p^4\ n1)$ and $H^+ + Kr^*(4p^5\ n1)$, are open at E = 15.6 eV, their effect only shows up at reduced angles $\tau \gtrsim 700$ eV.deg (i.e. $\theta \gtrsim 40$ deg at E = 15.6 eV) which are well outside the angular range of occurence of the rainbow features. Hence, these additional channels are unlikely to be the source of the discrepancy between the present theoretical results and the data of Weise et al (1971). We have incidentally found that the " experimental potential " extracted by these authors from their own results could not reproduce the data of Champion et al (1970) at lower energy (E = 6 eV).

3.3. Quantal cross sections for near resonant charge transfer.

The charge transfer differential cross sections, calculated in the four - state LCAO - SCF approach (see 3.1.a), at a E = 100 eV are shown along with experiment (Sec 2.2.) in fig. 10. A valid comparison between theory and experiment should be confined to reduced scattering angles $\tau < 700$ eV deg where the scattering is free from the effects induced by the neglected $H^+ + Kr^*$ and $H^* + Kr^+$ channels. Nevertheless the theoretical results are only in qualitative agreement with experiment as to the general trend of the low frequency oscillations in the cross sections. In addition to the incorrect description of the relative importance of the $^2P_{3/2}$ (A) and $^2P_{1/2}$ (B) cross sections, poor agreement is found in comparing (see Table I) the theoretical

total charge transfer cross sections with the data of Koopman (1967). Since charge transfer into the neglected channels is not large enough (Andreev et al. 1966) to explain such discrepancies, it is concluded that the failure of the LCAO - SCF approach is most probably caused by our neglection of radial dynamical coupling (fig. 8). If this is true, the above defects should disappear in the diabatic three - state PVB approach since this radial coupling is altogether taken into account in the potential coupling induced by the electronic hamiltonian (Kubach and Sidis 1976). Results of the three - state PVB calculations (fig 11a and 11b) indeed show improvement upon those of the LCAO - SCF approach. The $^2P_{1/2}$ cross section (ρ_B) is comparatively enhanced especially at small angles and the ratio between the $^2P_{1/2}$ and the $^2P_{3/2}$ cross sections is better reproduced in a wide angular range (τ <700 eV.deg).

When comparison is made with experiment, it should be kept in mind that the finite angular resolution of the apparatus washes out the high frequency oscillations seen in the theoretical differential cross sections. In order to illustrate this effect, the calculated cross sections at E = 100 eV(Fig.10,11a)have been convoluted over angle by assuming a gaussian apparatus function having a 0.2 deg full-width at half-maximum. The result of this treatment (Fig. 12,see also Fig. 5) more clearly illustrates the agreement of the PVB results with experiment. Complementary check of the quality of the theoretical results may be obtained from table I where the calculated PVB total charge transfer cross sections are compared with the experimental data of Koopman (1967).

As to the oscillations in the differential cross sections they are due to both " rainbow " and " Stueckelberg - Demkov " interferences . Indeed , the occurence of a " semi-localized " transition region around R_c (Sec. 3.1.b) provides a similar situation to that encountered in curve crossing problems. In the semi-classical picture, the interference is generated in the second outward passage accross the transition region after phases have been developed along the relevant potentials inside R_c. In the present case the ground state

actually seen to occur in the differential cross sections at reduced scattering angles $\tau \lesssim 350$ eV. deg. (see e. g. the elastic and ρ_A cross sections of Fig. 11). The Stueckelberg-Demkov interferences which are already present and superimposed upon the rainbow structure, at small angles, clearly emerge at $\tau > 400$ eV. deg., i. e. beyond the primary rainbow located at $\tau_R = 300$ eV. deg. (see Sec. 3.2). For $\tau > 700$ eV. deg. these structures are destroyed in the experimental cross sections due to absorption effects into various $H^+ + Kr^*$, $H^* + Kr^+$ and $H + Kr^{+*}$ channels. Of course, the above interference pattern is further complicated by the secondary $^2P_{1/2} \longleftrightarrow {}^2P_{3/2}$ fine structure transitions.

The structures seen in the H^+ - Ar near resonant charge transfer cross sections ($\rho_{A,B}$ in Fig. 7) can be interpreted on analogy with the above discussion for the H^+ - Kr case. In particular, the occurence of a maximum around $\tau \simeq 300$ eV. deg.(*) supports the interpretation of this feature as due to a rainbow effect caused by the well in the ground state potential curve (Champion et al. 1970 , Rich et al, 1971, Weise et al. 1971). The next structure at larger τ can be ascribed as a member of the Stueckelberg - Demkov oscillation pattern.

4. TOTAL CROSS SECTIONS FOR NEAR RESONANT CHARGE TRANSFER IN THE H^+ + Ar, Ne, He COLLISIONS.

The successful treatment of charge transfer in the H^+ + Kr collision within the PVB approach as deduced from the Demkov model (Sec. 3.1. b) suggests an extension of the same ideas to charge transfer in the lighter H^+ + RG systems. Since spin - orbit effects are small in these systems, only a two state approximation is needed. Furthermore, as the two-state charge transfer problem has extensively been investigated

---

(*) Footnote : The angular threshold for charge transfer has been confused with the rainbow structure by Sidis (1972). As a consequence an incorrect estimate of the critical transition region was obtained (See further discussions in Sec. 4).

in the literature, enough knowledge is available to avoid both lengthy molecular (LCAO or VB) calculations and numerical work on coupled equations. In the impact parameter treatment (IPM) of the collision, only the energy difference and the coupling between the two relevant states are required. Since the charge transfer model, summarized in Sec. 3.1.b., calls essentially for an atomic description, the relevant energy curves are nearly parallel and separated by the resonance energy defect ΔE. According to that picture, the charge exchange interaction between the states is governed by the assymptotic behaviour of the two orbitals involved in the charge transfer process. Consequently in the transition region around R_c the charge exchange interaction can be written as (Demkov 1964) :

$$H_{12}(R) = A \exp(-\lambda R) \tag{1}$$

and R_c is determined by (Stueckelberg 1932)

$$H_{12}(R_c) = \Delta E/2 \tag{2}$$

Various formulae, based on the study of the interaction of two atoms at large internuclear distances, have been proposed to determine the exponent λ in eq (1) :

$$\lambda = 0.5 \left(\sqrt{2I_H} + \sqrt{2I_{RG}}\right), \text{ (Smirnov 1968)} \tag{3a}$$

$$\lambda = \text{Min}\left(\sqrt{2I_H}, \sqrt{2I_{RG}}\right), \text{ (Demkov 1964)} \tag{3b}$$

$$\lambda = 0.43 \left(\sqrt{2I_H} + \sqrt{2I_{RG}}\right), \text{ (Olson } \underline{\text{et al}}\text{. 1971, Olson 1972)} \tag{3c}$$

where I_H and I_{RG} are the ionization potentials (in atomic units) of H and that of the rare gas respectively. However, it is easily shown (e. g. Kubach 1976), that when I_H and I_{RG} are different, it is the smallest of the ionization potentials (i. e. I_H) which governs the decrease of H_{12} at large R (eq. 3 b). Consequently in all the forthcoming discussions, λ will be taken equal to $\sqrt{2I_H} = 1.a_o^{-1}$.

To determine the preexponential factor A in eq (1) we have relied on the following assumptions (see e. g. Johnson et al. 1972) : (i) in the considered two state approximation the energy separation ΔE and V(R) between diabatic and adiabatic energy curves respectively satisfy the relation

$$V(R) = \left(\Delta E^2 + 4H_{12}^2 (R) \right)^{1/2} \qquad (4)$$

(ii) The diabatic energy curves V_D (R) are just screened Coulomb potential functions (Johnson et al. 1972)

$$V_D (R) = Z_{RG} \exp (- \lambda R) / R \qquad (5)$$

where Z_{RG} is the rare gas nuclear charge.

Knowing the ground state potential curve of the $(H - RG)^+$ system, either from low energy scattering experiments (Champion et al 1970, Weise et al. 1971, Rich et al. 1971) or from ab-initio calculations (e.g. Michels 1966, Green et al. 1954, Wolniewicz 1965, Peyerimhoff 1965, Roach and Kuntz 1970, Sidis 1972), equations (4) and (5) allow the determination of A (method a). If both the ground state and the charge exchange adiabatic energy curves are known (as in e. g. the $(H - He)^+$ system)then formula (4) alone allows the determination of both A and λ by a fitting procedure (method b). Alternatively, Olson et al (1971) suggested another expression (method c) to determine H_{12} :

$$H_{12} (R) = 0.5\sqrt{I_H I_{RG}} \left(\sqrt{2I_H} + \sqrt{2I_{RG}}\right) R \exp (-0.43 (\sqrt{2I_H} + \sqrt{2 I_{RG}})R) \quad (6$$

Knowing ΔE and H_{12} one could use the result of the Demkov model (1964) to determine the total charge transfer cross sections. However, it has been shown by Olson (1972) that more accurate cross sections could be obtained by scaling the numerical IPM results of the two-state charge transfer problem. The total charge transfer cross section Q as a function of the proton energy ($E = \frac{1}{2} m v_o^2$) can then be simply evaluated as :

$$Q = \frac{1}{2} \pi R_c^2 Q^* \qquad (7$$

where the universal function Q^* of the variable

$$\delta^{-1} = 2 \lambda v_o / \pi \Delta E \qquad (8$$

has been plotted and tabulated by Olson (1972). In the above formulae m and v_o are respectively the mass of the proton and the initial collision velocity.

4.1. Applications

4.1.1. H^+ + Ar

Refering to the work of Johnson et al. (1972) who used method (a), the critical internuclear distance is found to be $R_c = 5.2\ a_o$. This value agrees with that obtained from quantal calculations (Sidis 1975) involving an LCAO - SCF approach similar to that discussed in Sec. 3.1.a. The total cross sections based on equations (7) and (8) are shown in Fig. 13. The results agree satisfactorily with the experimental data of Koopman (1967), Stedeford and Hasted (1955) and Stier and Barnett (1956) in a wide energy range ($0.1\ keV \leqslant E \leqslant 10\ keV$). This agreement strongly encourages the application of the same method to the lighter systems of the H^+-RG sequence.

4.1.2 H^+ - Ne

Choosing $\lambda = 1\ a_o^{-1}$ and using method (a) we determine from the data on the $(H\text{-}Ne)^+$ ground state potential energy curve (Rich et al. 1971) the value $R_c = 3.8\ a_o$. The total charge transfer cross section, obtained as described above, is shown in Fig. 14. Satisfactory agreement with experiment is found at low proton energies ($E \leqslant 10$ keV). The discrepancy observed above E = 10 keV reflects the breakdown of the two state molecular approach neglecting momentum transfer of the exchanged electron. Allowance for momentum transfer is known to result

in a comparatively strong reduction of the cross sections at high velocities (Mc Dowell and Coleman 1970).

4.1.3. H^+ - He.

Proceeding in the same way as above (method (a)) one obtains for the H^+ - He system $\lambda = 1\ a_o^{-1}$, $R_c = 2.5\ a_o$. This value of R_c is just that predicted by Green and Johnson (1966) using a different procedure. This parametrization yields the cross section labelled(a) in Fig. 15. By using method (b) (eq. 4) in conjunction with the adiabatic potential energy curves of Michels (1966) one obtains the charge exchange interaction shown in Fig. 16. This interaction yields the values $R_c = 2.465\ a_o$, $\lambda = 0.875\ a_o^{-1}$. With this alternative parametrization one obtains the cross section labelled (b) in Fig. 15. According to the works of Olson et al (1971) and Olson (1972) (method c) the charge exchange interaction could be written as :

$$H_{12} = 0.787\ R \exp(-1.006\ R)$$

which determines the values $R_c = 2.08\ a_o$ and $\lambda = 1.006\ a_o^{-1}$ (eq. 3c). These parameters yield the cross-section labelled (c) in Fig 15. Comparison with experiment, at the lowest collision energies, does not allow to decide which parametrization is best. However, the scatter of the theoretical predictions is more clearly seen at higher energies where it appears that method (c) tends to underestimate the cross section . This feature was also found in the H^+ - Ar, Ne cases and is mainly due to the underestimation of R_c by the formula proposed by Olson et al. (1971) for H_{12}.

As in the case of the H^+ - Ne collision the departure of the present theoretical results from the experimental curve at high energy is most probably caused by the failure of the two-state molecular model neglecting momentum transfer.

5. CONCLUSIONS

The T.O.F. measurements reported in these series of papers enabled the determination of differential cross section for some charge transfer processes of the H^+ + Xe, Kr, Ar systems. Among these processes near resonant charge exchange is well isolated and has been submitted to detailed experimental and theoretical investigations. The outstanding new result of this study is the determination of the $^2P_{1/2}$ and $^2P_{3/2}$ contributions to the near resonant charge exchange process in H^+ + Kr, Xe at moderate energies ($E < 600$ eV). An additional important conclusion of the present theoretical analysis is that these processes are primarily induced, at large R, by purely electronic interactions between two diabatic $^1\Sigma^+$ states having an almost atomic description. Fine structure transitions and polarization phenomena then occur as secondary processes. This scheme is easily viewed within the PVB treatment which we consider to be a convenient and valuable method for handling similar problems in other systems. Finally, extension of these ideas, which stem from the work of Demkov, in conjonction with simple model interactions and with Olson's universal cross section provides a cheep and powerful means for calculating total charge transfer cross sections as it has been illustrated for the H^+ + Ar, Ne, He cases.

REFERENCES

Abignoli M., Barat M., Baudon J., Fayeton J. and Houver J.C., 1972, J. Phys. B : Atom Molec. Phys. 5, 1533 - 53.

Andreev E.P., Ankudinov V.A., Bobashev S.V., 1966 Sov. Phys. JETP 23, 375-82

Barat M. and Lichten W. 1972, Phys. Rev. A 6, 211-29

Bates D.R., 1962, Discuss. Faraday Soc. 33, 7-13

Becker M. and Scharmann A. 1969, Z. Naturf. 24, 854-5

Benoit C., Kubach C., Sidis V., Pommier J. and Barat M., 1975 IXth International Conference on the Physics of Electronic and Atomic Collisions (Abstracts of Papers) edited by J.S. Risley and R. Geballe (University of Washington 1975) 1, 169-70

Brenot J.C. Pommier J., Dhuicq D. and Barat M., 1975, J. Phys. B : Atom. Molec. Phys. 8, 448-59

Champion R.L., Doverspike L.D., Rich W.G. and Bobbio S.M. 1970, Phys. Rev. A 2, 2327-34

Crothers D.S.F., 1971, Adv. Phys., 20, 405-51
1973, J. Phys. B. : Atom. Molec. Phys. 6, 1418-25

De Heer F.J, Schutten J. and Moustafa H. 1966, Physica 32, 1766-92

Demkov Yu N., 1964, Sov. Phys. JETP, 18, 138-42

Fleischmann H.H. and Young R.A., 1967, Phys. Rev. Letters 19, 941-3

Gordon R.G. 1969, J. Chem. Phys. 51, 14 -25
1971, Meth. Comput. Phys. 10, 81-109

Green T.A., Stanley H.E. and Von Chien Chiang 1965, Helv. Phys. Acta 38, 109

Green T.A. and Johnson R.E., 1966, Phys. Rev. 152, 9-17

Green T.A., Michels H.H., Browne J.C. and Madsen M.M., 1974, J. Chem. Phys. 61, 5186-97

Johnson R.E., Carlson C.E. and Boring J.W. 1972, Chem. Phys. Letters 16, 119-22

Koopman D.W. 1967, Phys. Rev. 154, 79-85

Kubach C., Sidis V and Durup J., 1975, J. Phys. B : Atom. Molec. Phys. 8, 1129-38

Kubach C., Benoit C., Sidis V., Pommier J. and Barat M. 1976, in press in J. Phys. B : Atom. Molec. Phys.

Kubach C. and Sidis V., 1976, in press in Phys. Rev. A

Kubach C., 1976, Thèse d'Etat : work in progress

Mc Dowell M.R.C. and Coleman J.P.1970, Introduction to the theory of Ion-Atom Collisions (North Holland Publishing Company) Amsterdam, London, 155-62.

Mappleton R.A. 1972, Theory of Charge exchange. Wiley Inter- Science p.215

Michels H.H., 1966, J. Chem. Phys. 44, 3834-50

Nikitin E.E., 1968, Chem. Phys. Letters 2, 402-4
1969, Comm. Atom. Molec. Phys. 1, 111-5
1970, Comm. Atom. Molec. Phys. 2, 118-23

Olson R.E., Smith F.T. and Bauer E. 1971, Appl . Opt. 10, 1848-55

Olson R.E., 1972, Phys. Rev. A 6, 1822-30

O'Malley T.F., 1969, J. Chem. Phys. 51 322,34

Peyerimhoff S. 1965, J. Chem. Phys. 43 998-1010

Rich W.G., Bobbio S.M., Champion R.L. and Doverspike L.D. 1971, Phys. Rev. A, 4, 2253, 60

Rapp D. and Francis W.E. 1962, J. Chem. Phys. 37, 2631-45

Rich W.G., Bobbio S.M., Champion R.L. and Doverspike L.D. 1971, Phys. Rev. A4 2253-60

Rosen N. and Zener C., 1932, Phys. Rev. 40, 502-

Shakeshaft R. and Macek J. 1973, Phys. Rev. A 7, 1554-9

Sidis V. 1972, J.Phys. B : Atom. Molec. Phys. 5, 1517-28

Sidis V. 1975, Thèse de Doctorat d'Etat (Université Pierre et Marie Curie)

Smirnov B.M. 1968 Atomic Collisions and Elementary Processes in Plasma (Atomizdat , Moscow).

Smith F.T. 1969, Phys. Rev. A. 179 111-23

Stedeford J.B. and Hasted J.B. 1955, Proc. Roy. Soc. A 227 466.

Stern B., Gauyacq J.P. and Sidis V., to be published

Stier P.M. and Barnett C.F. 1956, Phys. Rev. 103, 8986-907

Stueckelberg ECG.1932, Helv. Phys. Acta 5, 369-422

Weise H.P., Mittmann H.P., Ding A. and Henglein A. 1971, Z. Naturf. 26 a, 1112-28

Williams G.J. and Dunbar D.N. 1966, Phys. Rev. 149, 62-69

Wolniewicz L. 1965, J. Chem. Phys. 43 1087-91.

Collision energy (eV)	Calculated cross sections σ_2 (present work) ($\AA^2$)			experimental cross section σ_2 (Koopman (1967) ($\AA^2$)
	LCAO - SCF calculations		PVB calculations	
100	$^2P_{3/2}$	11.7	16.9	20.5
		sum 13.7	sum 20.7	
	$^2P_{1/2}$	2.0	3.8	
200	$^2P_{3/2}$	10.9	17.5.	26.0
		sum 13.5.	sum 22.1	
	$^2P_{1/2}$	2.6.	4.6.	

Table I. Comparison between experimental and calculated total charge exchange cross sections for the H^+ + Kr collision.

FIGURE CAPTIONS

Fig. 1 : Energy loss spectra of D atoms scattered from the D^+ + Kr collision at a beam energy : E = 300 eV.
(The corresponding collision energy for the H^+ + Kr system is E = 150 eV)
The labeling of the peaks is defined in the text.

Fig. 2 : Energy loss spectrum of H atoms scattered from the H^+ + Kr collision (at E = 750 eV and = 1.5 deg.) showing the charge exchange excitation processes C and D (see text).

Fig. 3 : Energy loss spectrum of H atoms scattered from the H^+ + Ar collision at E = 520 eV, $\theta = 1.5°$

Fig. 4 : Experimental reduced differential cross section for the near resonant charge transfer processes of the H^+ + Kr collision at beam energies of :

(a) E = 100 eV, (b) E = 150 eV, (c) E = 200 eV, (d) E = 250 eV
Figures (a) and (c) also show the comparison between the sum of the present cross sections for processes A and B (0) with the data of Fleischmann and Young (1967) (×)

Fig. 5 : Experimental relative population of the A ($Kr^+ {}^2P_{1/2}$) and B ($Kr^+ {}^2P_{3/2}$) channels at various energies as a function of the reduced scattering angle. The curve (——) deduced from fig. 12 b shows the relative population calculated (at E = 100 eV) in the PVB treatment discussed in Sect.3 of the text.

Fig. 6 : Experimental reduced differential cross sections for the near resonant charge transfer process $\rho_{A,B}$ and for the charge exchange excitation processes ρ_C and ρ_D, at a beam energy of E = 600 eV, of the H^+ + Kr collision.

Fig. 7 : Experimental reduced differential cross sections for the near resonant charge transfer process ($\rho_{A,B}$) and for the charge exchange excitation processes (ρ_C and ρ_D) of the H^+ + Ar collision at a beam energy E = 520 eV, the triangles are data from the measurements of Abignoli et al (1972).

Fig. 8 : $^1\Sigma^+$ potential energy curves and coupling schemes involved in the theoretical treatments of the H^+ + Kr collision

(a) LCAO - SCF representation. The d/dR couplings have been neglected.

(b) PVB representation : The basis change from the PVB-diabatic states (region I) to the SCF - CI adiabatic states (region II) is carried out at R_D. The charge transfer transition takes place around R_c.

For clarity the $^3\Pi$ state also involved in the fine structure transition is not shown.

ig. 9 : Differential cross sections for the scattering of H^+ by Kr at low energies.

(a) Elastic cross sections at E = 6 eV (center of mass) : (...) data from the work of Champion et al. (1970), (-) present semi-quantal JWKB - one - state calculation involving the adiabatic ground state of the $(H - Kr)^+$ molecule ion.

(b) Results at E = 15.8 eV (laboratory). Elastic : (...) data from the work of Weise et al. (1971), (---) present semi-quantal JWKB - one - state calculation , (—) three state quantal PVB calculations. Near resonant charge transfer : (—) quantal $^2P_{3/2}$-PVB cross section, (---) quantal $^2P_{1/2}$-cross section.

ig. 10 : Reduced differential cross sections from the four state quantal SCF calculations for near resonant charge transfer processes :

(—) ρ_A ($^2P_{3/2}$), (---) ρ_B ($^2P_{1/2}$) at a beam energy E = 100 eV.

The present experimental data (▲ for ρ_A and • for ρ_B) are shown for comparison. The experimental cross section $_A$ is arbitrarily normalized to theory around 300 eV. deg.

ig. 11 : Reduced differential cross section from the three state quantal PVB calculation. (·····) elastic (▬) ρ_A and (---) ρ_B : (a) E = 100 eV, (b) E = 200 eV. The experimental data have the same nomenclature and normalization as in fig. 10.

Fig. 12 : Theoretical reduced differential cross sections after angular convolution ($\Delta\theta$ = 0.2 deg). of : (a) fig. 10, (b) fig. 11a; same nomenclature and normalization as in fig.10.

Fig. 13 : Total charge transfer cross sections for H^+ + Ar collisions full line : present theoretical calculation, (■) Stedeford and Hasted (1955), (+) Williams and Dunbar (1966), (*) de Heer et al (1966), (▲) Koopman (1967).

Fig. 14 : Total charge transfer cross sections for H^+ + Ne collisions full line : present theoretical calculation, (■) Stedeford and Hasted (1955), (+) data from both Williams and Dunbar (1966) and Stier and Barnett (1956).

Fig. 15 : Total charge transfer cross sections for the H^+ + He collisions. Present theoretical calculations : (a) $\lambda = 1 a_o^{-1}$, $R_c = 2.5 a_o$, (b) $\lambda = 0.875\ a_o^{-1}$, $R_c = 2.465\ a_o$, (c) $\lambda = 1\ a_o^{-1}$, $R_c = 2.08\ a_o$.

(■) Stedeford and Hasted (1955), (x) Stier and Barnett (1956), (+) Williams and Dunbar (1966), (*) de Heer et al. (1966), (⊕) calculations of Green et al. (1965), (—) Bates two state method calculation (Mapleton 1972).

Fig. 16 : Charge exchange interaction obtained from the ab initio. calculations of Michels (1966) for H^+ + He. Half the energy defect ($\Delta E/2$) defines the critical distance R_c.

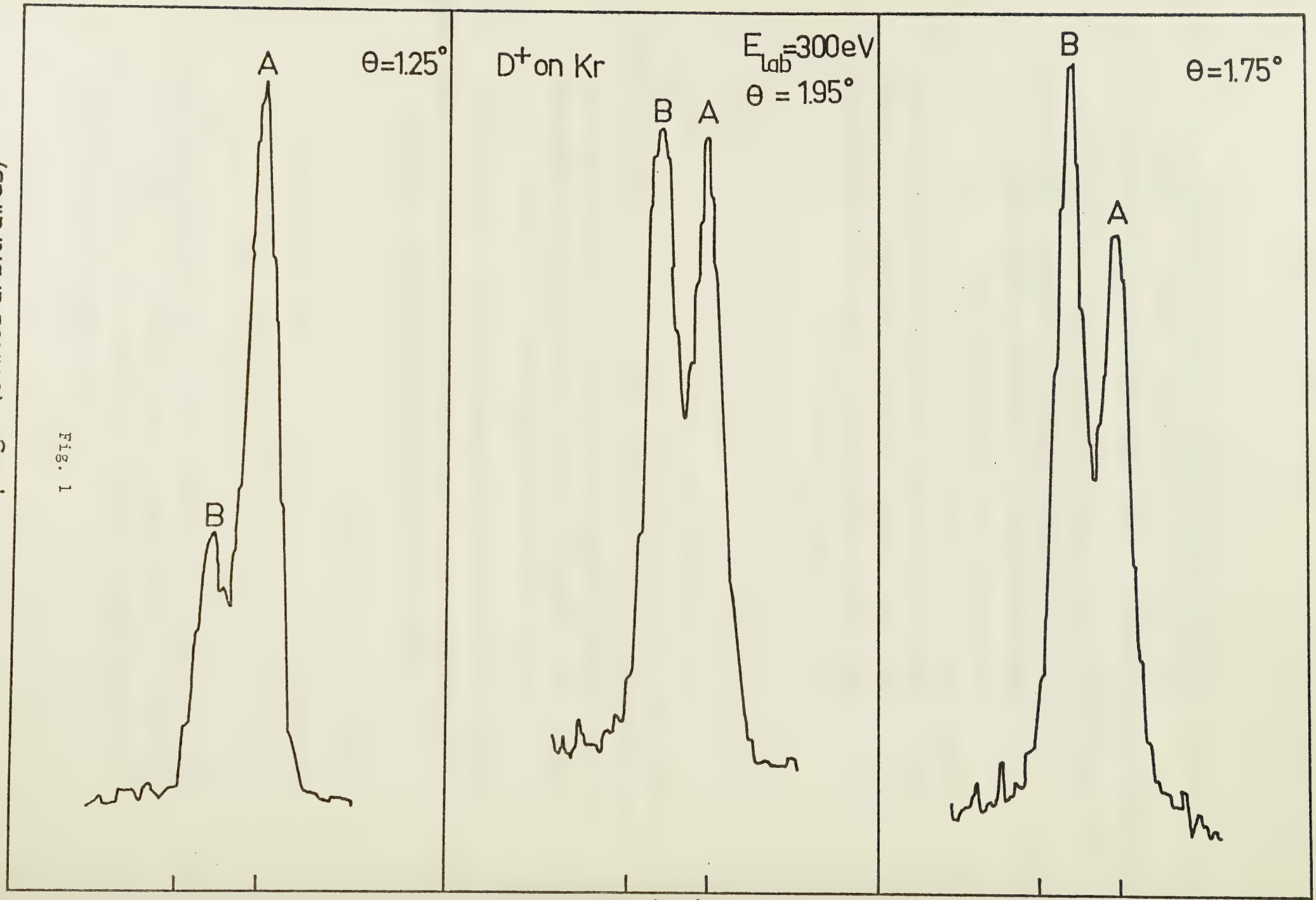

D+ on Kr
E lab=300eV
θ = 1.95°
θ=1.25°
θ=1.75°
A
B
B A
B
A
Flux de comptage (Unités arbitraires)
ΔE (eV)

Fig. 1

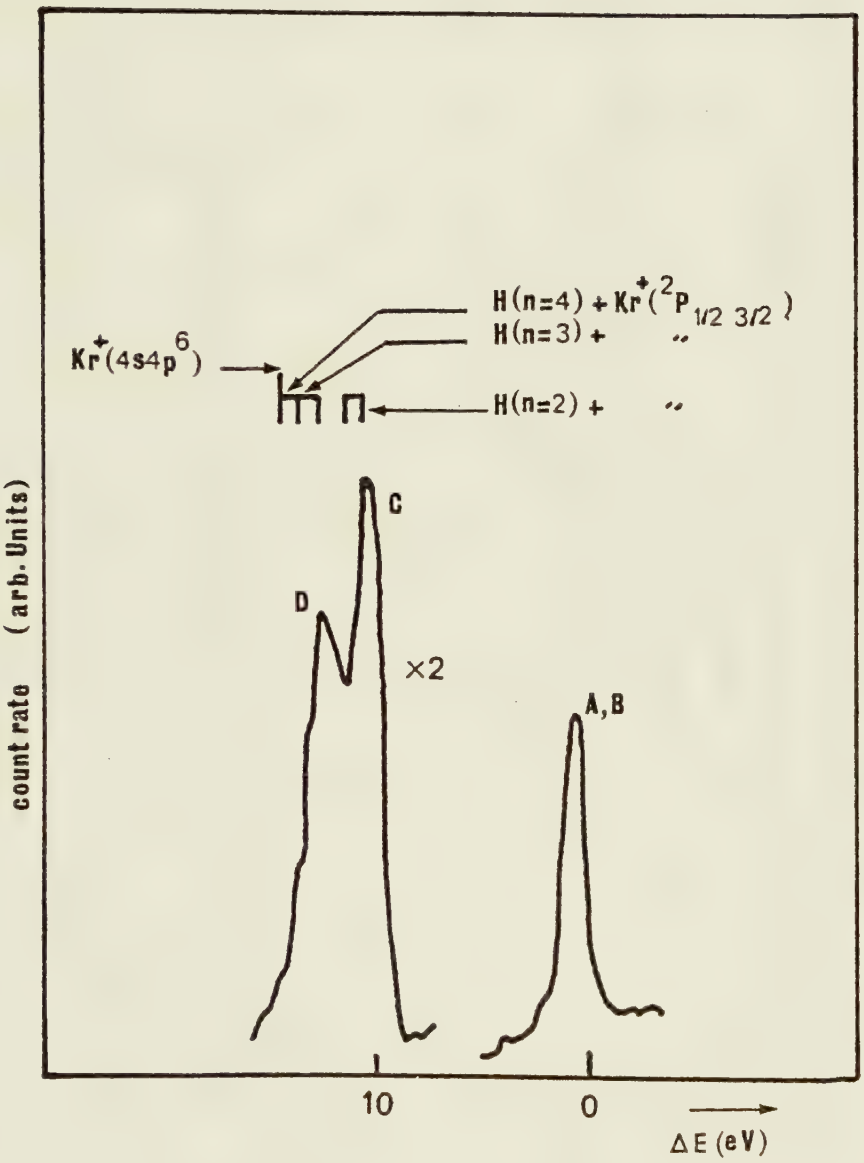

H(n=4) + Kr+(2P1/2 3/2)
H(n=3) + "
H(n=2) + "
Kr+(4s4p6)
C
D
×2
A,B
count rate (arb. Units)
10
0
ΔE (eV)

Fig. 2

H+ + Ar
E lab = 520 eV
C
A, B
D
×16
Taux de comptage (Unités arbitraires)
10
0
ΔE (eV)

Fig. 3

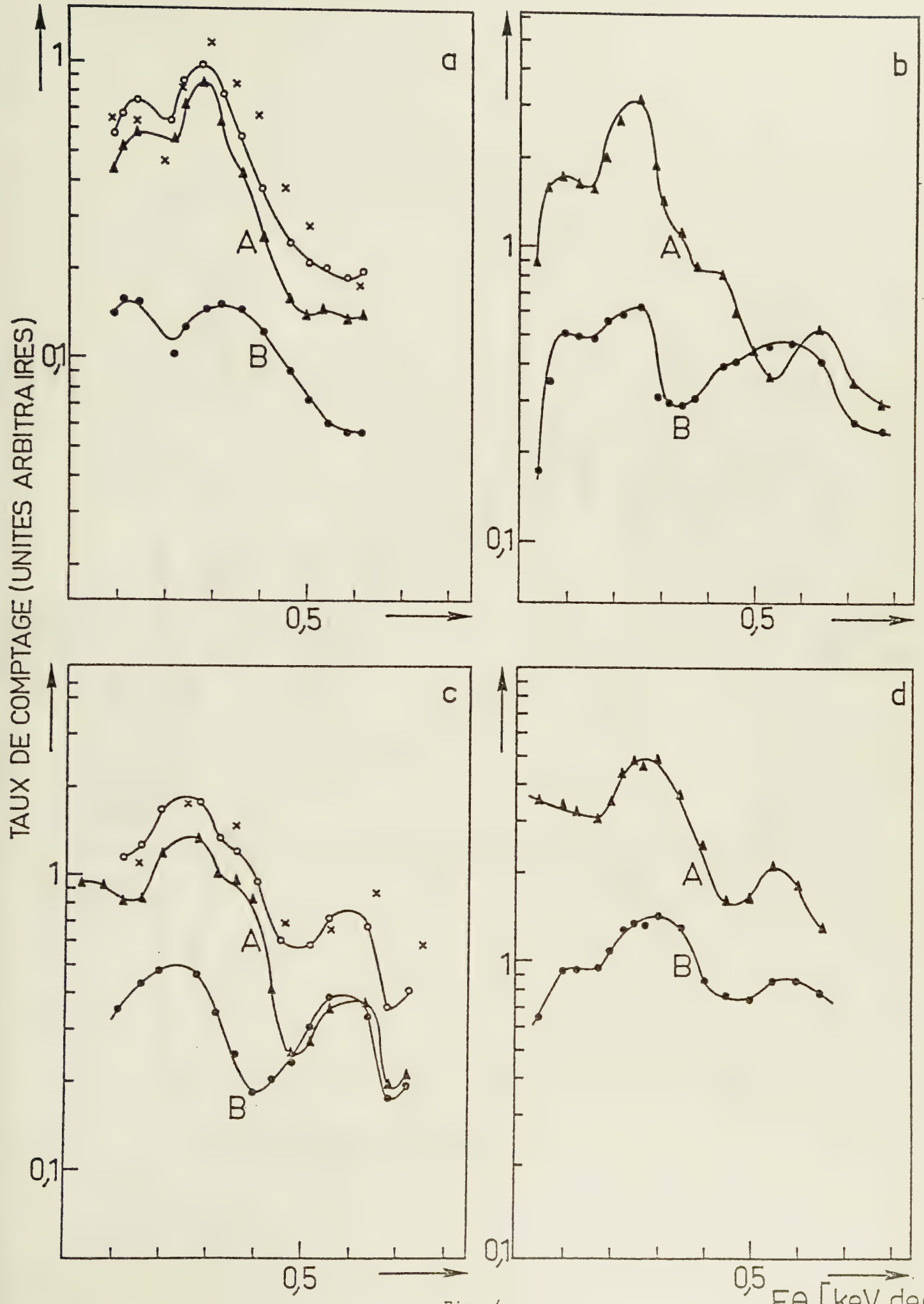

a
b
c
d
A
B
1
0,1
0,5
TAUX DE COMPTAGE (UNITES ARBITRAIRES)
Eθ [keV deg]

Fig. 4

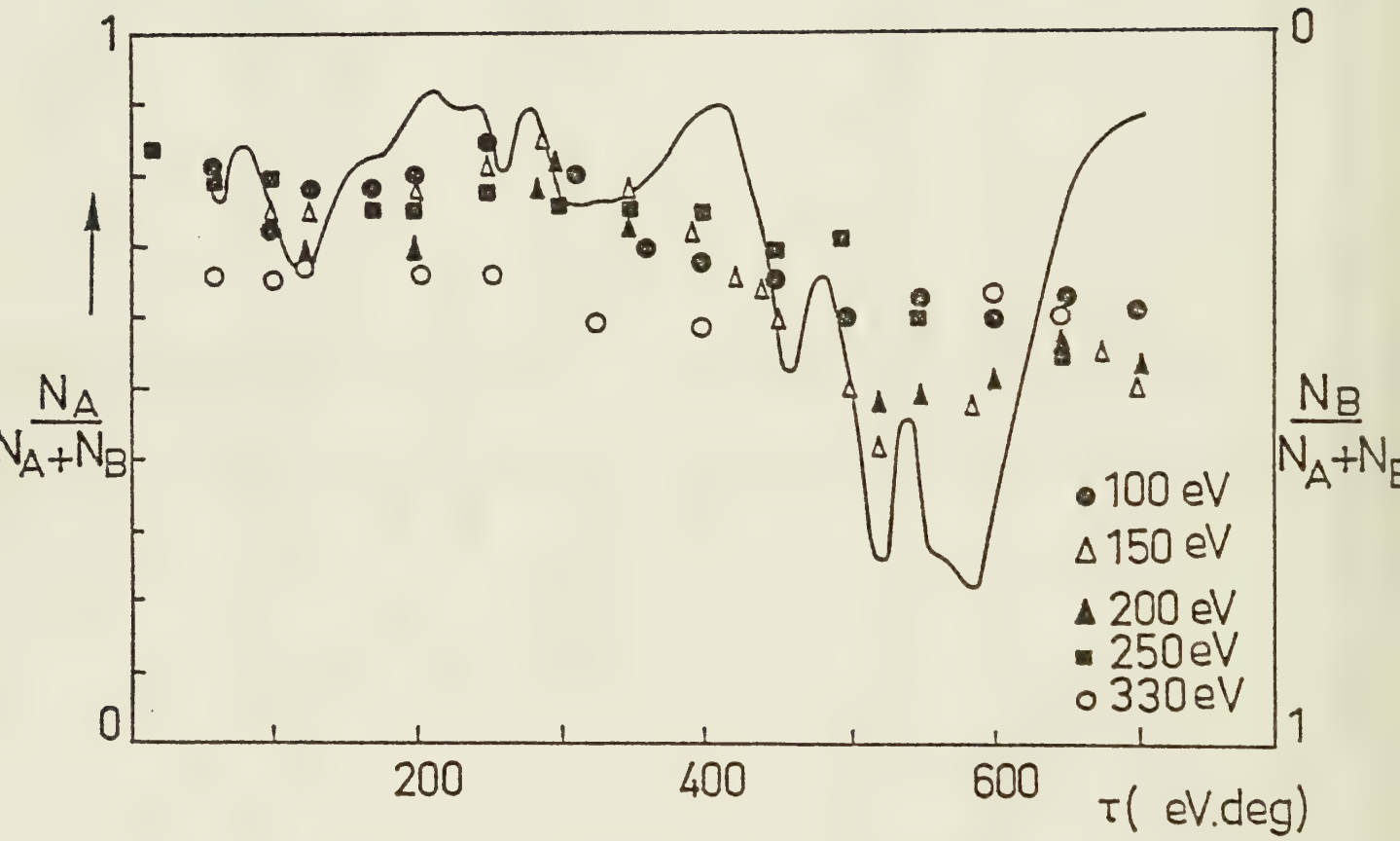

1
0
$\frac{N_A}{N_A+N_B}$
$\frac{N_B}{N_A+N_B}$
100 eV
150 eV
200 eV
250 eV
330 eV
0
1
200
400
600
τ(eV.deg)

Fig. 5

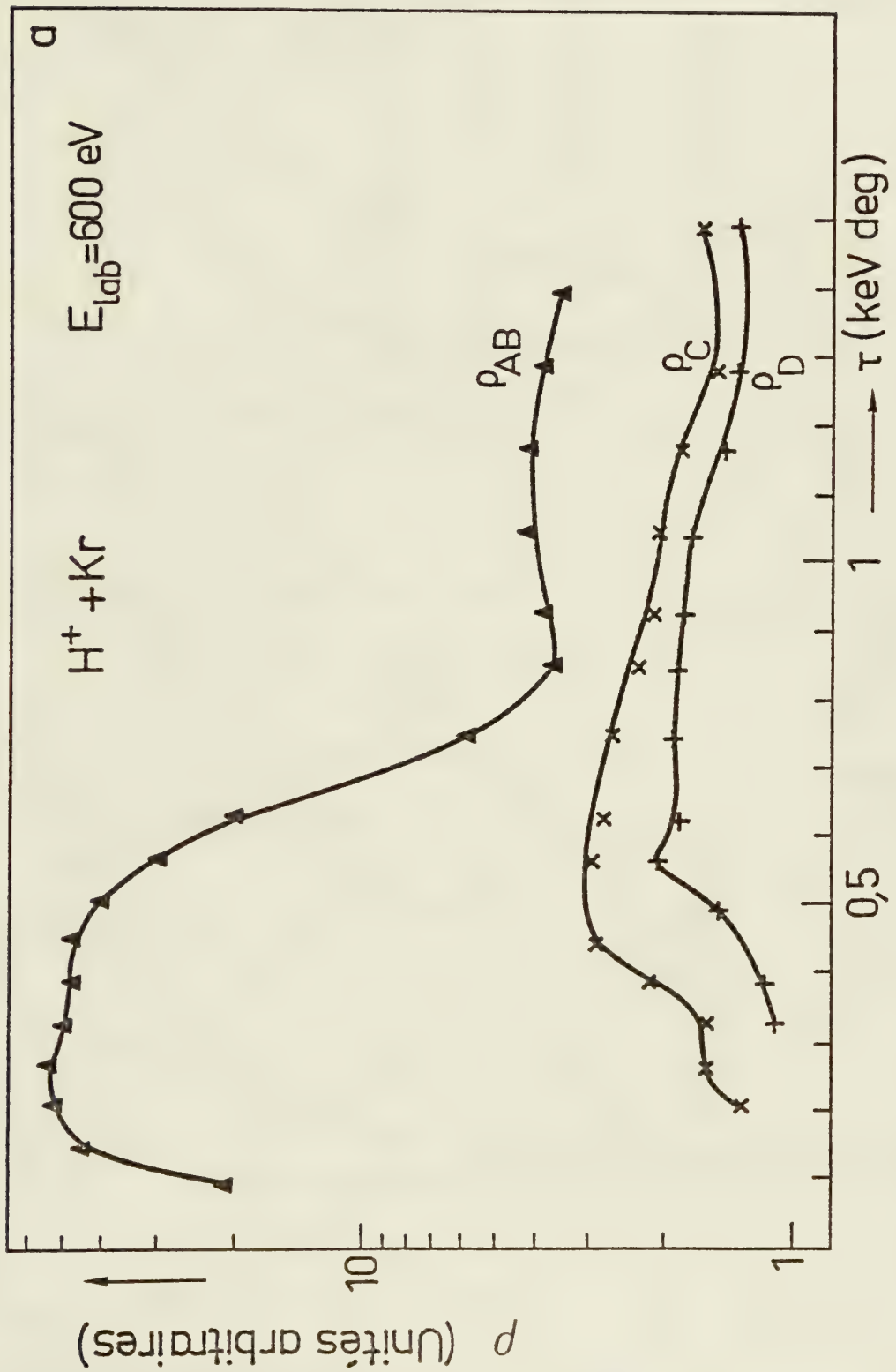

a
E_{lab}=600 eV
H^++Kr
ρ_{AB}
ρ_C
ρ_D
10
1
0,5
1
τ (keV deg)
ρ (Unités arbitraires)

Fig. 6

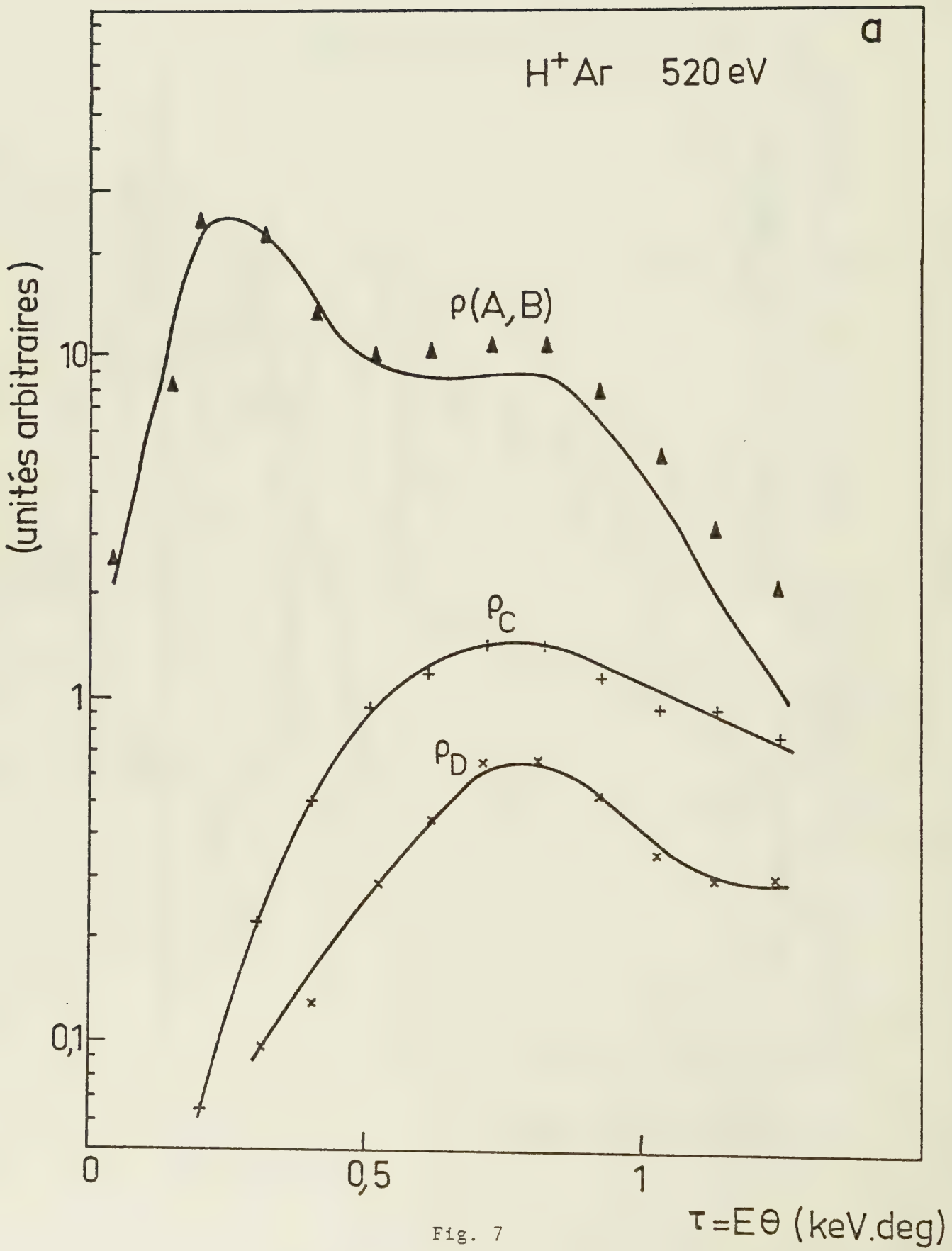

a
H+Ar 520 eV
ρ(A,B)
ρC
ρD
(unités arbitraires)
10
1
0,1
0
0,5
1
τ=Eθ (keV.deg)

Fig. 7

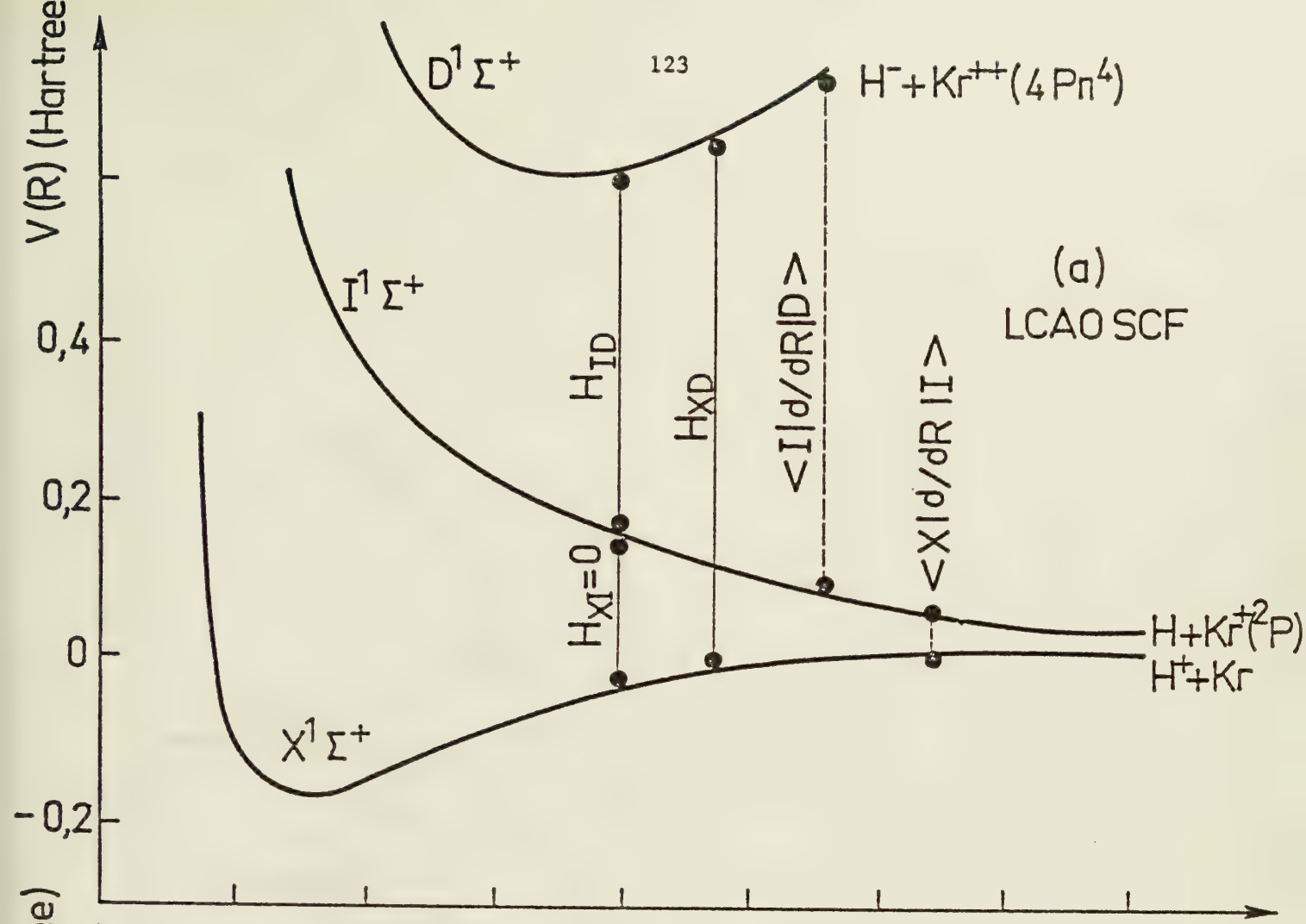

V(R) (Hartree)
D¹Σ⁺
H⁻+Kr⁺⁺(4Pπ⁴)
I¹Σ⁺
(a)
LCAO SCF
H_ID
H_XD
<I|d/dR|D>
<X|d/dR|I>
H_XI=0
H+Kr⁺(²P)
H⁺+Kr
X¹Σ⁺
0,4
0,2
0
-0,2

Fig. 8

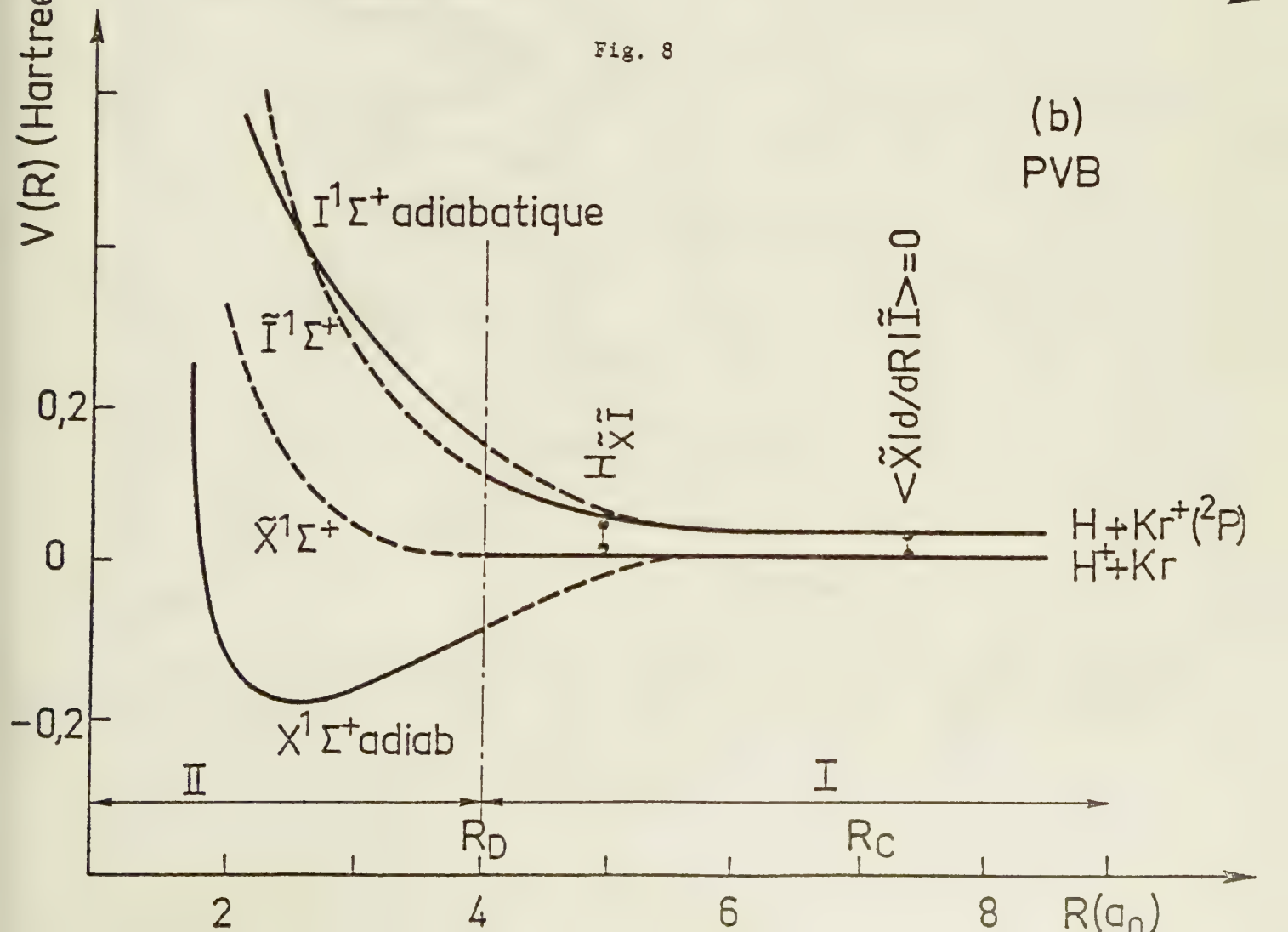

V(R) (Hartree)
(b)
PVB
I¹Σ⁺adiabatique
Ĩ¹Σ⁺
X̃¹Σ⁺
H_X̃Ĩ
<X̃|d/dR|Ĩ>=0
H+Kr⁺(²P)
H⁺+Kr
X¹Σ⁺adiab
II
I
R_D
R_C
0,2
0
-0,2
2
4
6
8
R(a₀)

Fig. 9a

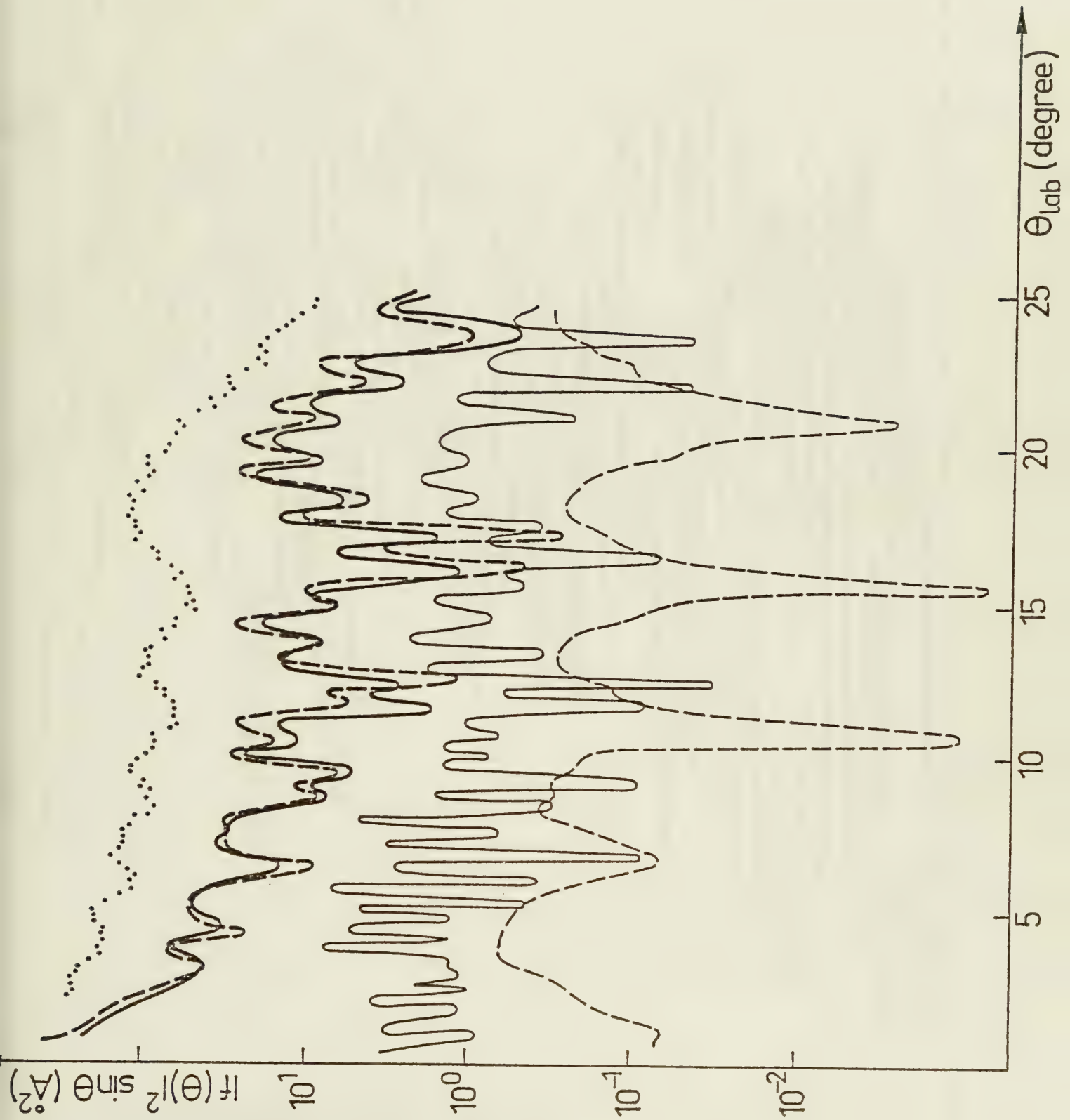

$|f(\theta)|^2 \sin\theta$ (Å^2)
10^{1}
10^{0}
10^{-1}
10^{-2}
5
10
15
20
25
θ_{lab} (degree)

Fig. 9b

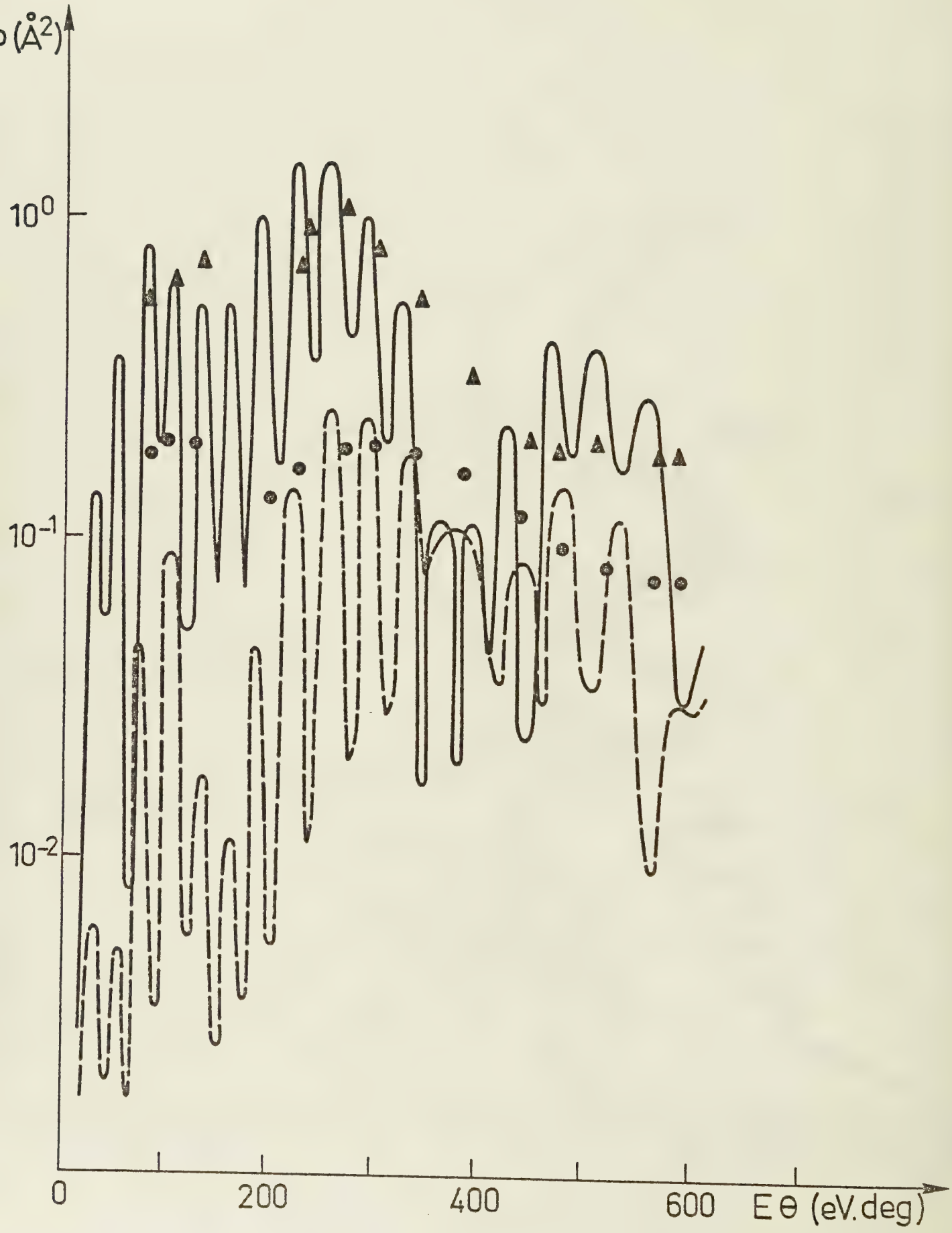


Fig. 10

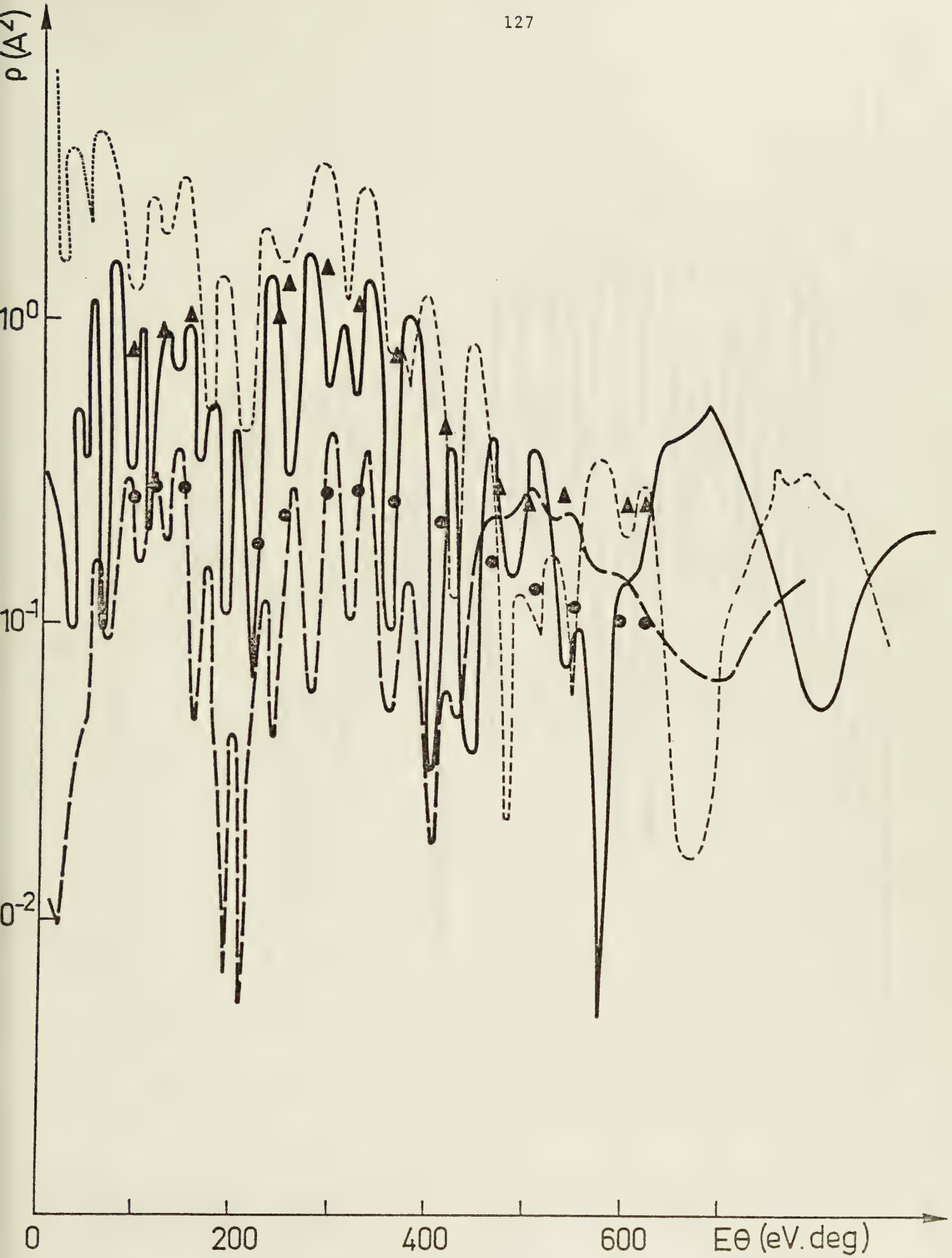


Fig. 11a

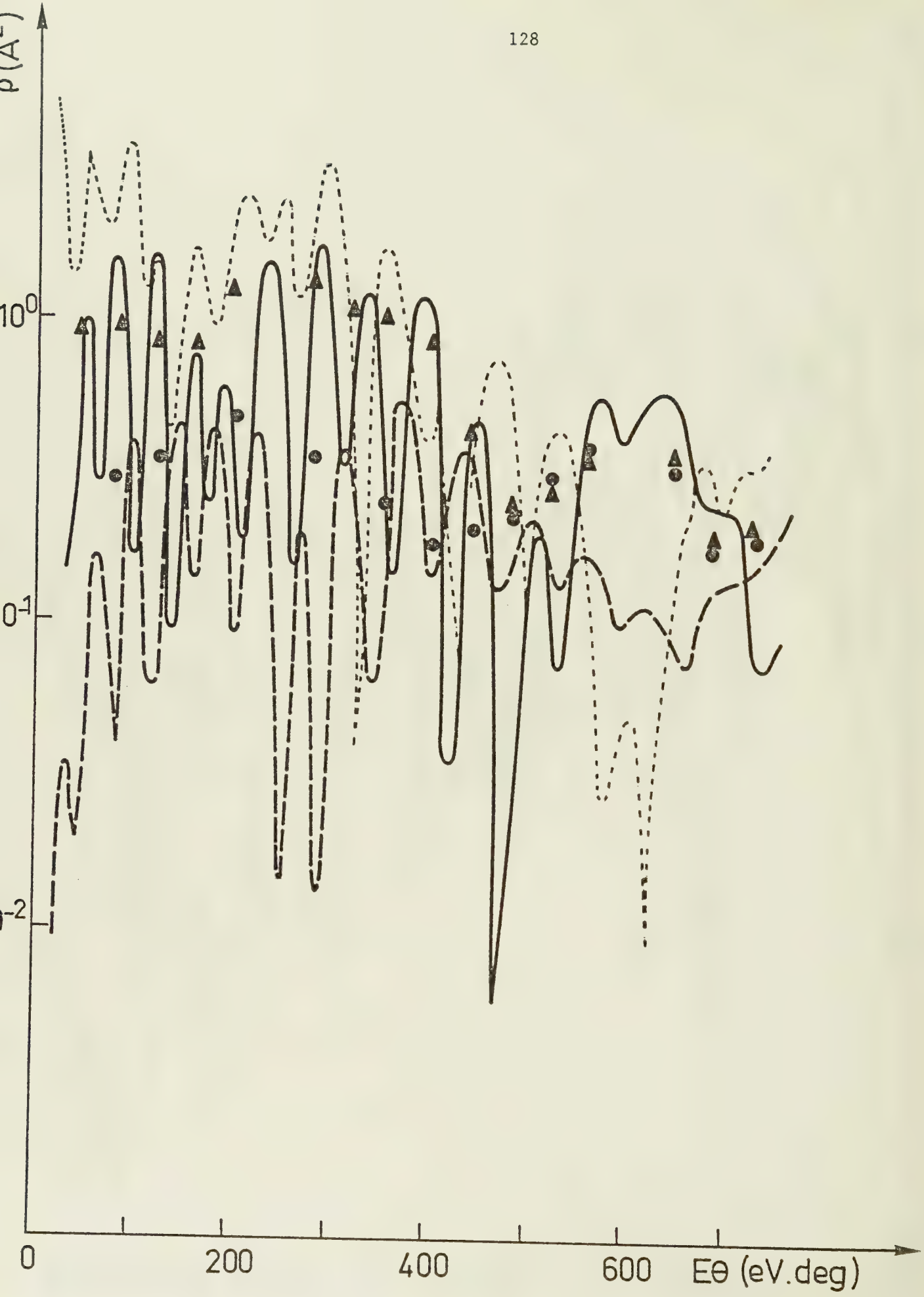


Fig. 11b

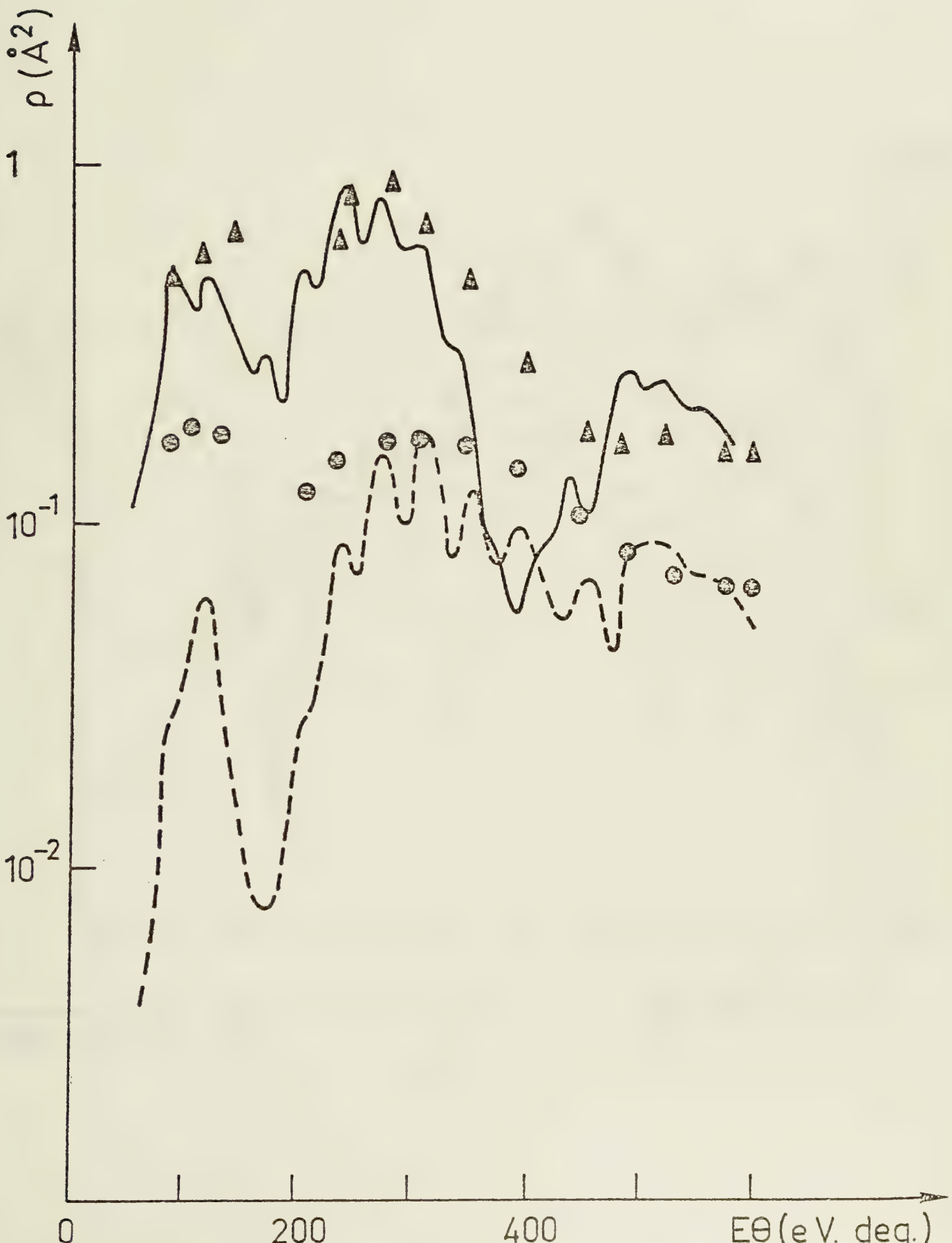


Fig. 12a

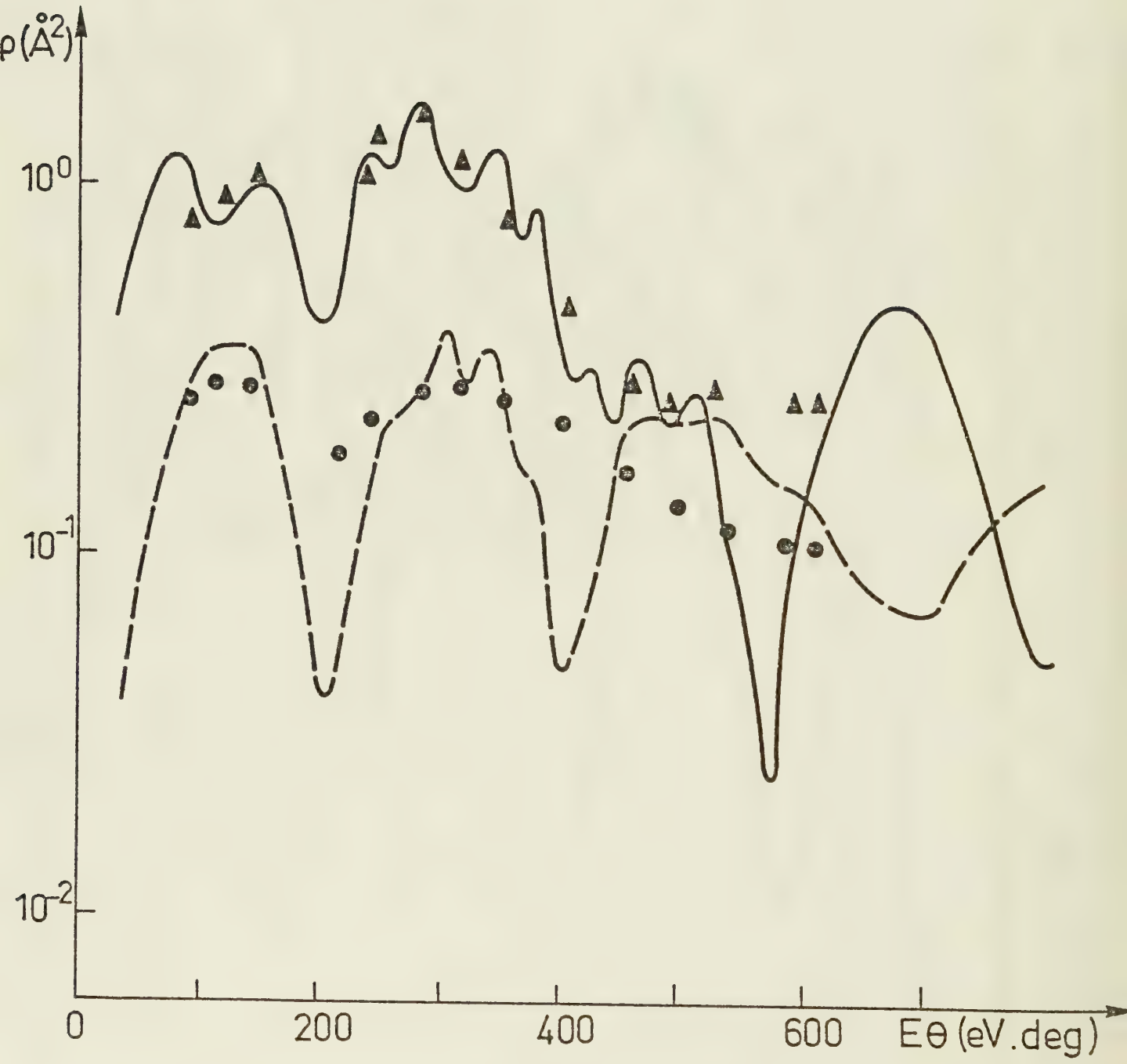


Fig. 12b

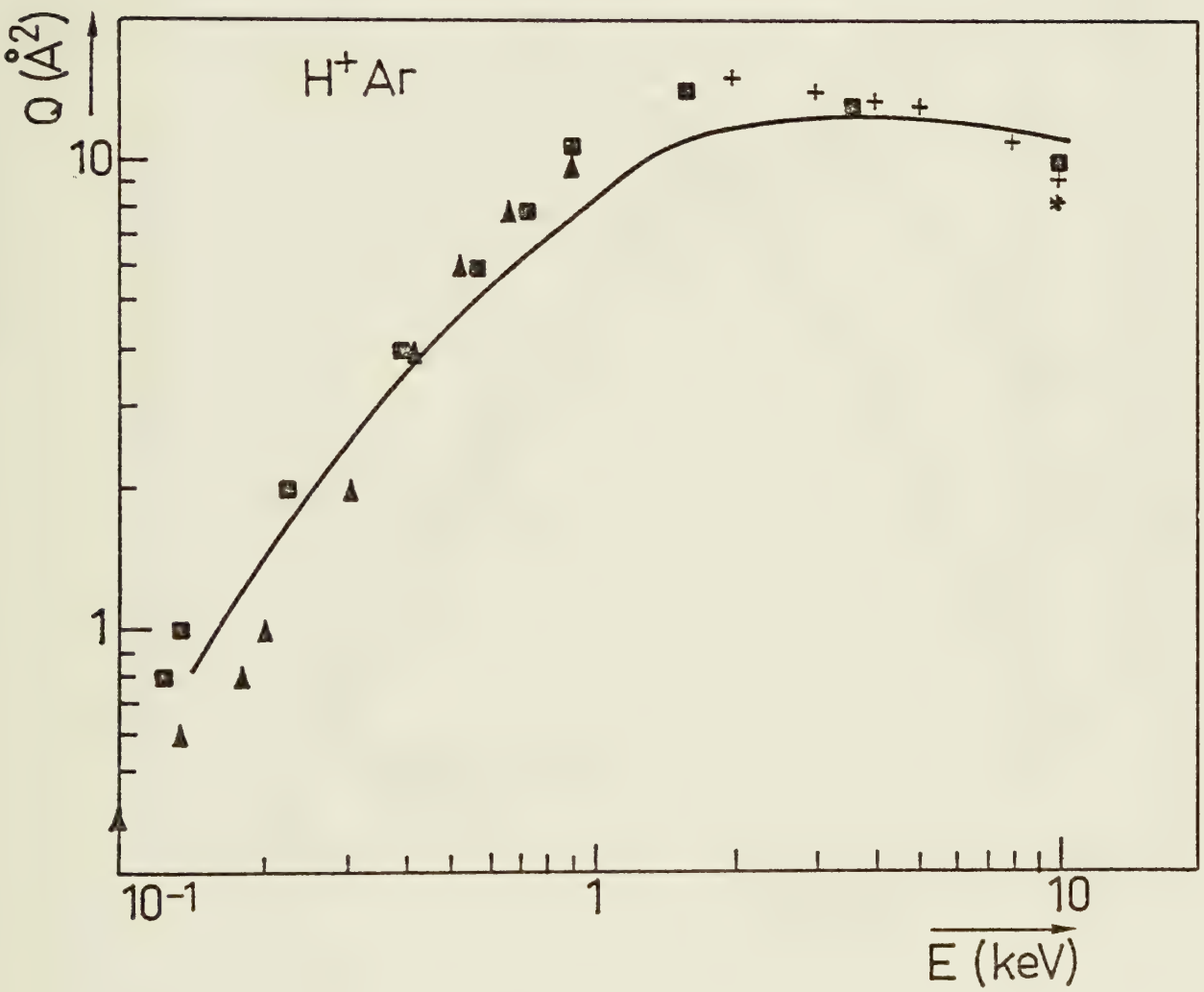


Fig. 13

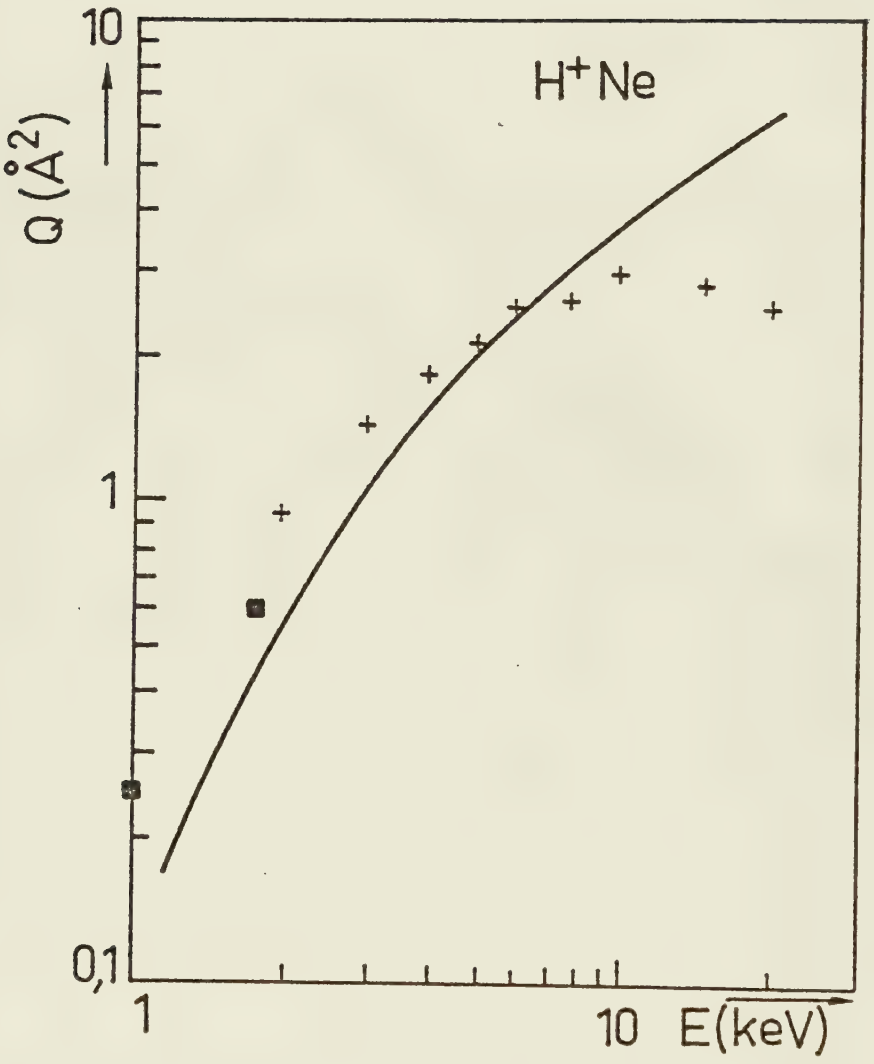


Fig. 14

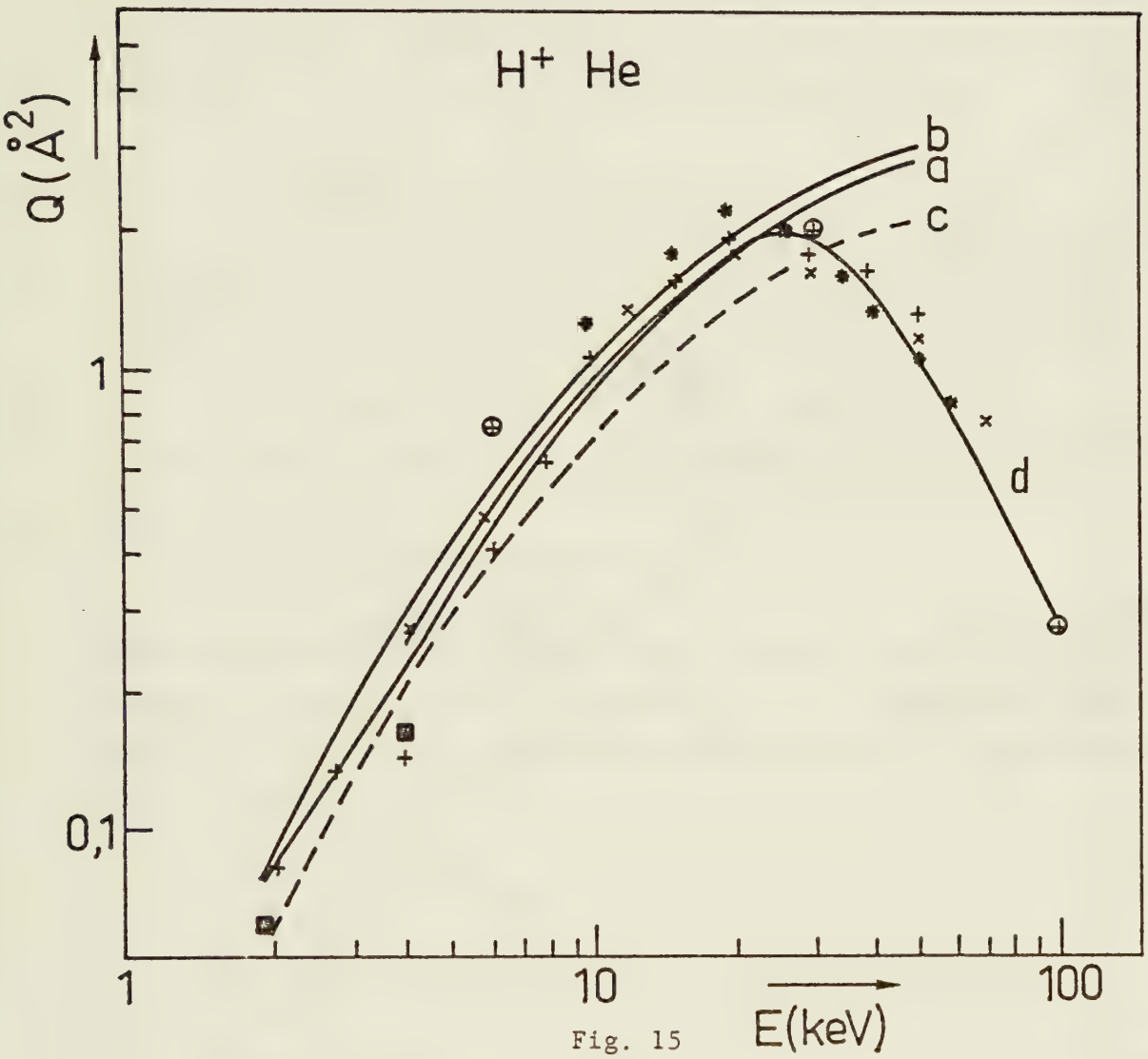


Fig. 15

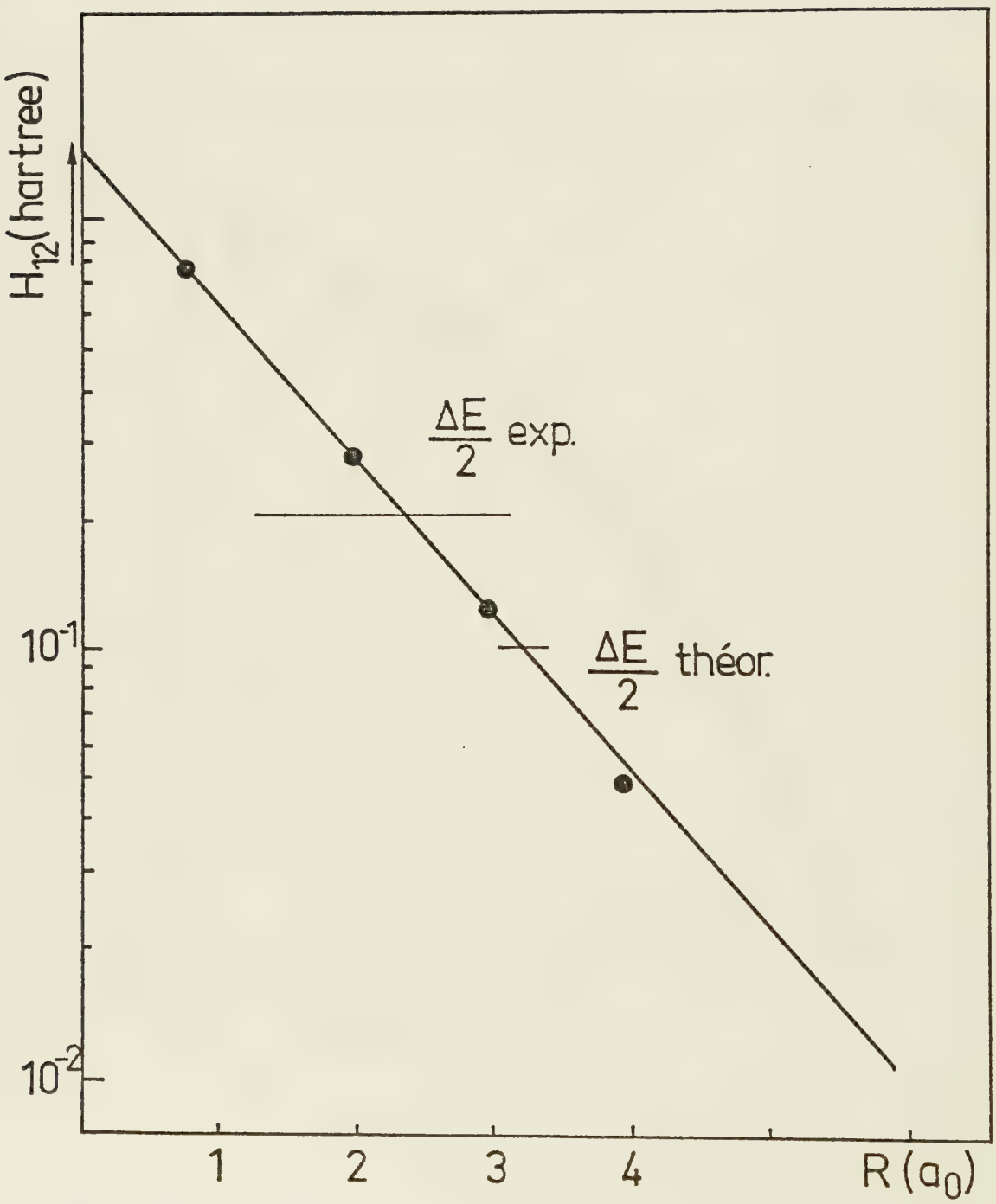

H_{12}(hartree)
10^{-1}
10^{-2}
$\frac{\Delta E}{2}$ exp.
$\frac{\Delta E}{2}$ théor.
1
2
3
4
R (a_0)

Fig. 16

DISCUSSION ET COMMENTAIRES

1 - Dans la description LCAO - SCF de l'échange de charge quasi-résonnant dans les collisions $H^+ + Kr$, l'état diexcité $D\,^1\Sigma^+$ joue bien le rôle d'un état virtuel. En effet, les probabilités de transition P_D vers cet état sont extrêmement petites, alors que les probabilités d'échange de charge quasi-résonnant sont notables. Ainsi, à 200 eV, on obtient $P_D < 1$ % pour tout paramètre d'impact alors que la probabilité d'échange de charge vers l'état $^2P_{3/2}$ de Kr^+ oscille entre 0 et 70 %.

2 - Probabilité d'échange de charge

Afin d'illustrer le comportement oscillatoire de la probabilité d'échange de charge, correspondant à des transitions semi-localisées, nous avons reporté (fig. 17) les probabilités P (b) d'échange de charge calculées à 100 eV pour la collision $H^+ + Kr$.

Nous avions prévu que les transitions responsables de l'échange de charge dans la collision $H^+ + Kr$ s'effectueraient autour de :

$$R_c = 7\ a_o \quad \text{(cf chapitre VII)}$$

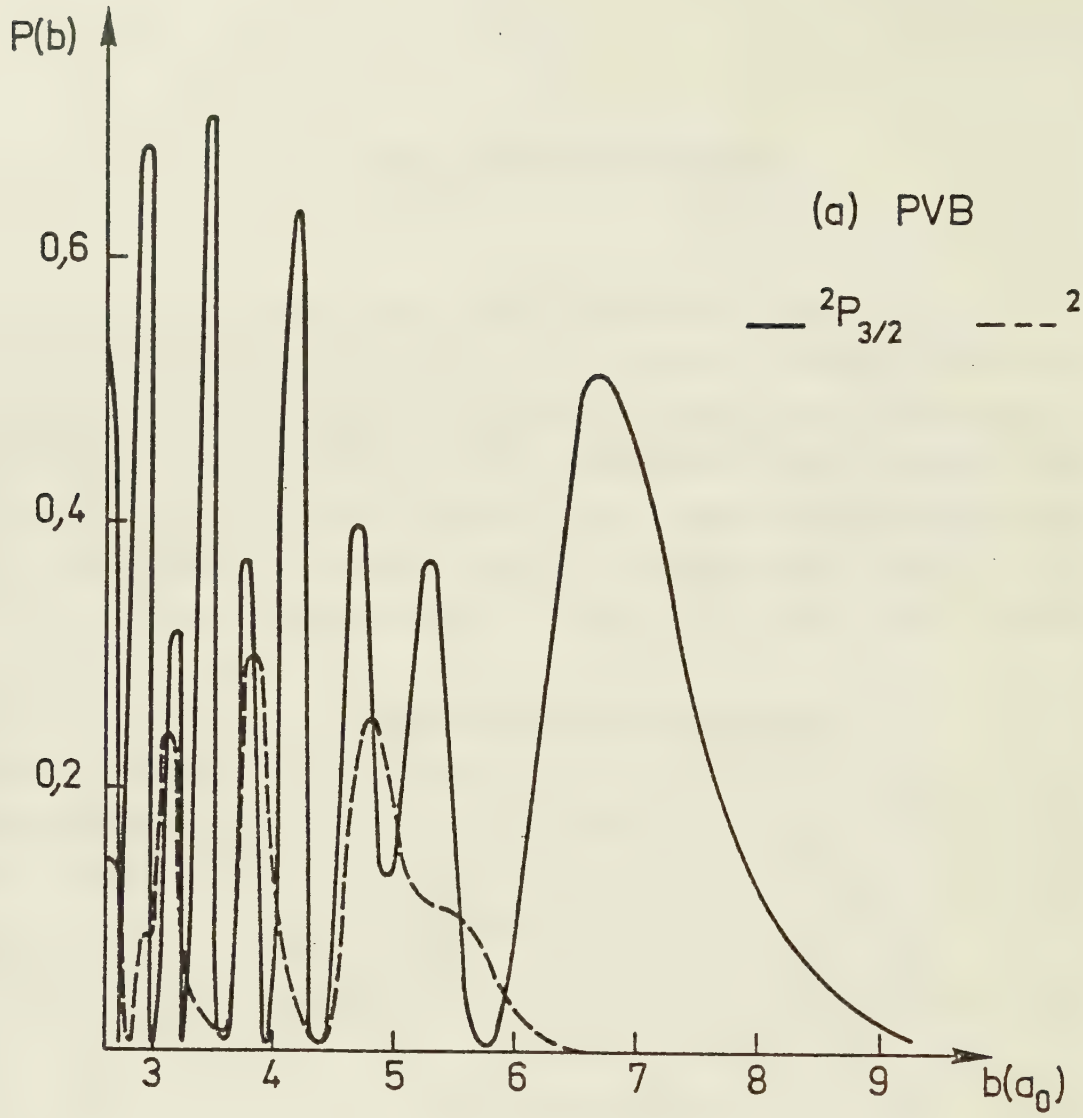
Cette valeur est obtenue en considérant les deux états $^1\Sigma^+$ de plus basse énergie. En fait, la prise en considération de l'intéraction spin-orbite conduit à des distances légèrement différentes pour les localisations des processus séparés :

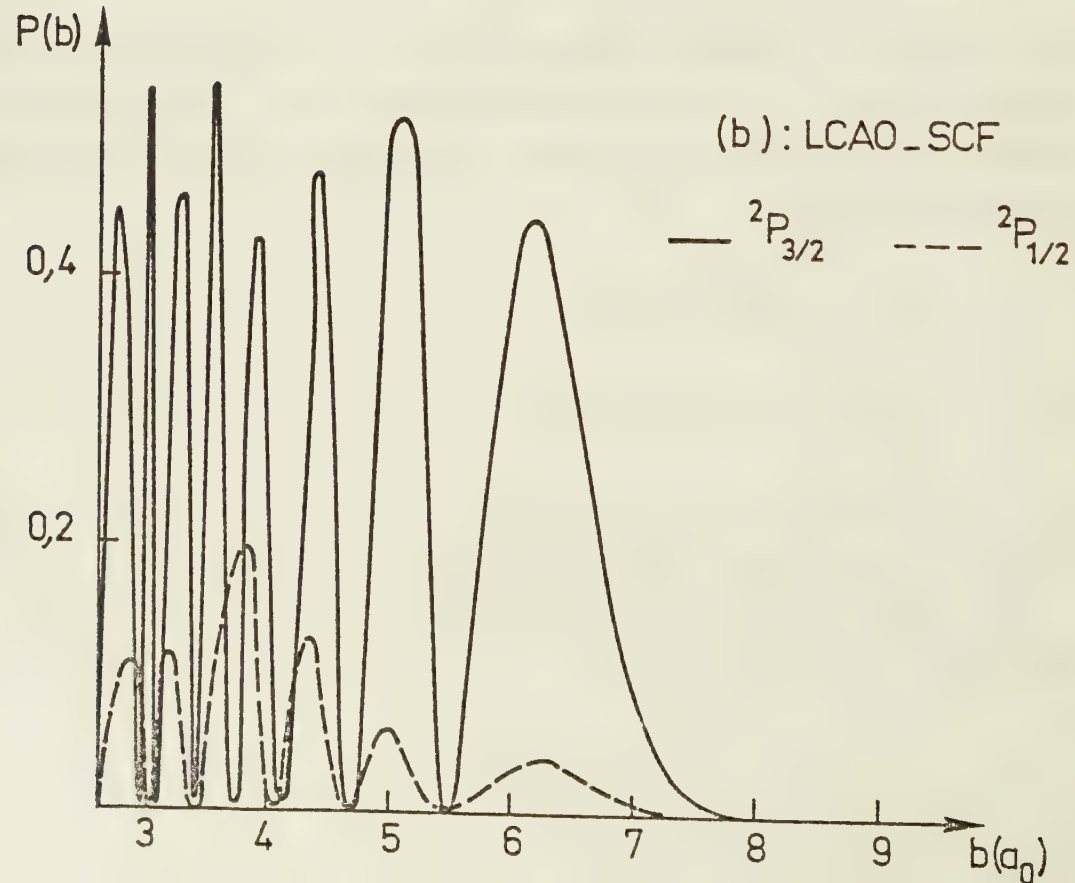
$$H^+ + Kr \rightarrow Kr^+ (^2P_{3/2}) + H$$

et $$H^+ + Kr \rightarrow Kr^+ (^2P_{1/2}) + H$$

Ceci est confirmé par les chutes des probabilités de transition observées dans le calcul PVB pour $b \gtrsim 9\ a_o$ et $b \gtrsim 6{,}5\ a_o$ respectivement (cf fig. 17).

La comparaison des probabilités d'échange de charge calculées à une même énergie de collision, dans les bases LCAO - SCF et PVB, permet de


P(b)
0,6
0,4
0,2
(a) PVB
$^2P_{3/2}$
$^2P_{1/2}$
3
4
5
6
7
8
9
b(a_0)


P(b)
0,4
0,2
(b) : LCAO_SCF
$^2P_{3/2}$
$^2P_{1/2}$
3
4
5
6
7
8
9
b(a_0)

comprendre l'origine des différences observées dans les valeurs des sections totales (cf tableau I).

En effet, dans l'expression de la section totale :

$$Q = 2\pi \int_{o}^{b_{max}} b.P(b)\, db$$

où b_{max} est tel que pour $b > b_{max}$ on a $P(b) \simeq 0$, les grands paramètres d'impact interviennent de façon prépondérante. Les valeurs de b_{max} observées pour le transfert de charge dans l'état $^2P_{3/2}$ de Kr^+ sont (cf fig. 17) respectivement de 9 a_o et de 7,5 a_o dans les calculs PVB et LCAO - SCF. On conçoit alors que la première approche conduise à une plus grande section efficace totale que la seconde.

Pour les processus intervenant à grandes distances internucléaires, le bon accord entre les sections efficaces totales calculées et les résultats expérimentaux indiquera que la distance critique R_c, où s'effectuent les transitions, a été correctement déterminée.

3 - Comportement asymptotique du couplage responsable de l'échange de charge : $A^+ + B \longrightarrow A + B^+$

Les deux états corrélés respectivement à $A^+ + B$ et $A + B^+$, diffèrent d'une spin-orbitale dans l'approximation mono-configuration. L'électron qui "traduit" l'échange de charge passe d'une orbitale moléculaire ϕ_B à une orbitale moléculaire ϕ_A. On peut, dans le calcul du couplage $\langle X \mid H_{el} \mid I \rangle$ à grande distance internucléaire, remplacer les orbitales moléculaires ϕ_A et ϕ_B par des orbitales atomiques X_A et X_B, et H_{el} par un hamiltonien décrivant le mouvement d'un électron dans le champ de deux noyaux écrantés. Cette méthode a été proposée par Gurnee et Magee /24/. On arrive ainsi à :

$$\langle X \mid H_{el} \mid I \rangle \underset{R\to\infty}{=} \left\langle X_A \left| -\frac{1}{2}\nabla^2 - \frac{\zeta_A}{r_A} - \frac{\zeta_B}{r_B} + \frac{\zeta_A \zeta_B}{R} \right| X_b \right\rangle \quad (9)$$

Afin d'éviter, dans le calcul de l'expression (9), la présence d'un terme d'énergie, il est préférable d'utiliser des orbitales orthogonales,

par exemple :

$$|\chi_A\rangle \quad \text{et}$$

$$|\tilde{\chi}_B\rangle = \frac{1}{\sqrt{1-S^2}} \left(|\chi_B\rangle - S\,|\chi_A\rangle \right) \text{ avec } S = \langle \chi_A \,|\, \chi_B \rangle$$

on obtient ainsi :

$$\langle \tilde{\chi}_B \,|\, H_{el} \,|\, \chi_A \rangle = \frac{1}{\sqrt{1-S^2}} \left(\langle \chi_B \,|\, H_{el} \,|\, \chi_A \rangle - S \langle \chi_A \,|\, H_{el} \,|\, \chi_A \rangle \right) \qquad (10)$$

et en utilisant la relation :

$$-\frac{1}{2}\nabla^2 - \frac{\zeta_A}{r_A} \,|\, \chi_A\rangle = E_A \,|\chi_A\rangle$$

et on aboutit finalement à :

$$\langle \tilde{\chi}_B \,|\, H_{el} \,|\, \chi_A \rangle = \frac{1}{\sqrt{1-S^2}} \left\{ \langle \chi_B \,|\, -\frac{\zeta_B}{r_B} \,|\, \chi_A \rangle - S \langle \chi_A \,|\, -\frac{\zeta_B}{r_B} \,|\, \chi_A \rangle \right\} \qquad (11)$$

On peut utiliser une approximation hydrogénoïde des orbitales atomiques /24/ et écrire à grande distance :

$$\chi_B \sim r_B^{n-1} \, e^{-\sqrt{2I_B} \cdot r_B}$$

$$\chi_A \sim r_A^{n-1} \, e^{-\sqrt{2I_A} \cdot r_A} \qquad (12)$$

Dans cette expression on n'a retenu que les termes d'ordre supérieur en r_A et r_B . Les exposants des exponentielles s'obtiennent en remarquant que, pour un atome hydrogénoïde, l'énergie (c'est-à-dire le potentiel d'ionisation) s'écrit :

$$|E| = \frac{1}{2} \frac{\zeta^2}{n^2}$$

Tous les termes de l'expression (11) peuvent alors être calculés en utilisant les coordonnées elliptiques ($\lambda = (r_A + r_B)\, R^{-1}$; $\mu = (r_A - r_B)\, R^{-1}$). On obtient après intégration sur ces coordonnées une série de termes de la forme :

$$A\ R^{a} \left(e^{-\sqrt{2I_A}\, R} + e^{-\sqrt{2I_B}\, R} \right) \qquad (13)$$

Si les potentiels d'ionisation de A et B sont très différents, c'est l'exponentielle qui décroît le plus lentement qui impose le comportement asymptotique du couplage. On obtient donc :

$$H_{12}(R) \sim A\, R^{a}.\ e^{-\sqrt{2I_m}\, R} \qquad (14)$$

où I_m désigne le plus petit des deux potentiels d'ionisation I_A, I_B.
Cette expression du couplage, au terme R^a près, intervient dans la théorie de l'échange de charge quasi-résonnant de Demkov /26/. Il convient de noter que l'on a déterminé ici le comportement asymptotique du couplage responsable de l'échange de charge. Il est possible que, dans le domaine de distances internucléaires où s'effectuent les transitions, les expressions de Smirnov /98/ ou de Olson et al /34/, données au paragraphe 4, soient mieux adaptées.

Dans le cas de l'échange de charge résonnant pour les collisions H^+ - H, le calcul développé ci-dessus est plus rigoureux et on arrive à une expression de type :

$$H_{12}(R) = A.R.e^{-R} \qquad (15)$$

(cf par exemple réf. /99/)

4 - Section totale "universelle" pour l'échange de charge quasi-résonnant

Afin d'éclairer la discussion du paragraphe 4, nous reproduisons ici la démarche suivie par Olson /32/ pour obtenir une section totale universelle pour les processus d'échange de charge.

On peut calculer la section totale d'échange de charge en utilisant l'expression de la probabilité de transition obtenue par Demkov /26/ :

$$P(b) = \operatorname{sech}^2 \left\{ \frac{\pi \Delta E(R_c)}{2 \lambda v(b)} \right\} \sin^2 \int_{-\infty}^{+\infty} H_{12}\, dt \qquad (16)$$

où $\lambda = \sqrt{2I_m}$ et où $v(b)$ désigne la vitesse radiale des noyaux dans la région de transition ($R \sim R_c$) :

$$v(b) = v_o \left(1 - b^2/R_c^2 \right)^{1/2}$$

On obtient, en remplaçant $\sin^2 \int_{-\infty}^{+\infty} H_{12}\, dt$ par sa valeur moyenne : 1/2, l'expression de la section totale :

$$Q = 4 \pi R_c^2 \int_1^{\infty} \frac{e^{-2\delta x}}{x^3 (1+e^{-2\delta x})^2}\, dx \qquad (17)$$

où $\delta = (\pi \Delta E)/2 \lambda v_o$ (ce résultat se retrouve rapidement en posant $x = (1 - b^2/R_c^2)^{1/2}$).

On remarque alors que la section réduite : $Q^* = \frac{Q}{\frac{1}{2}\pi R_c^2}$ est une fonction universelle de la vitesse "réduite" δ^{-1}.

En fait, la section totale étant dominée par la contribution des grands paramètres d'impact ($b \sim R_c$), pour lesquels la formule de Demkov n'est pas valable, l'expression (17) suggère qu'une relation $Q^* = f(\delta^{-1})$ existe mais ne permet pas de déterminer cette relation. Olson a construit la section efficace universelle réduite $Q^* = f(\delta^{-1})$ en calculant numériquement P(b), sans utiliser la formule de Demkov, pour diverses valeurs de paramètres v_o, R_c, λ .... Les points obtenus s'écartent de moins de 10 % d'une courbe moyenne universelle (cf fig. 1 réf. /32/).

Chapitre IX

DIABATIC STATES OF THE H^+ - Xe COLLISIONAL SYSTEM*

C. Kubach (•) and V. Sidis (:)

(•) Laboratoire des Collisions Ioniques, associé au C.N.R.S.
Bât. 420, Université de Paris-Sud, 91405 ORSAY - FRANCE.

(:) CMOA 23, rue du Maroc, 75019 PARIS - France
Present address : Laboratoire des Collisions Atomiques,
Bât. 220, Université Paris-Sud, 91405 ORSAY - FRANCE.

ABSTRACT :

Diabatic states of the H^+ - Xe collisional system have been calculated using the projected valence bond (PVB) method. The two lowest diabatic $^1\Sigma^+$ PVB states are found to cross at an internuclear distance R = 4.7 a_o. For collision energies E $\lesssim$ 1 KeV no transition takes place at this crossing since it is strongly avoided in the corresponding adiabatic energy curves. On the other hand it is shown that Demkov-type transitions occuring at larger distances (R $\simeq$ 6.7 a_o) are responsible for the near-resonant charge exchange processes in H^+ + Xe collisions. The PVB results, in conjunction with diabatic states for spin-orbit coupling, are used in quantum calculations of differential cross sections. The results are compared with previous theoretical and experimental data.

---

* à paraître J. Phys. B : octobre 1976.

The projected valence bond (PVB) method (Kubach and Sidis 1976) provides a simple way to obtain diabatic states (defined by Smith 1969) for charge exchange processes involving nuclei having very different masses. This approach has been proposed and developed in a study of the H^+ - Kr collisional system (Kubach and Sidis 1976). In this letter we present a brief account of results of the PVB method applied to the H^+ - Xe system.

The PVB states are written as Slater determinants :

$$\tilde{X}^1\Sigma^+ = |\sigma 1s_{Xe}\bar{\sigma}1s_{Xe} \ldots \sigma 5p_{Xe}\bar{\sigma}5p_{Xe}|$$

$$\tilde{I}^1\Sigma^+ = \frac{1}{\sqrt{2}}\left\{|\sigma 1s_{Xe}\bar{\sigma}1s_{Xe} \ldots \sigma 5p_{Xe}\,\bar{\sigma}1\tilde{s}_H| - |\sigma 1s_{Xe}\bar{\sigma}1s_{Xe} \ldots \bar{\sigma}5p_{Xe}\sigma 1\tilde{s}_H|\right\} \quad (1)$$

where $1\tilde{s}_H$ is a $1s_H$ atomic orbital orthogonalized to any Xe ground state atomic orbital ($1s_{Xe}$, ... ,$5p_{Xe}$). Assuming that the center of mass of the nuclei lies on the Xe nucleus it is easily shown that the $\tilde{X}$ and $\tilde{I}$ states satisfy $\langle \tilde{X} | d/dR | \tilde{I} \rangle = -\langle \tilde{I} | d/dR | \tilde{X} \rangle = 0$

The potential energy curves $\langle \tilde{X}\,^1\Sigma^+ | H_{el} | \tilde{X}\,^1\Sigma^+ \rangle$ and $\langle \tilde{I}\,^1\Sigma^+ | H_{el} | \tilde{I}\,^1\Sigma^+ \rangle$ (fig. 1) were calculated using subroutines of the Alchemy program written by Bagus et al (•). The two diabatic curves are nearly parallel at large R ($R > 6a_o$) and cross at $R = 4.7\ a_o$. From the Landau-Zener formula (Landau 1932, Zener 1932) for the transition probability at a curve crossing :

$$P = 1 - e^{\frac{-2\pi H_{12}^2}{v_R\ \Delta F}} \quad (2)$$

where v_R is the nuclear radial velocity, H_{12} the coupling and ΔF the absolute value of the difference in slopes at the curve crossing, one finds with the calculated values : $H_{12} = 0.09$ Hartree, $\Delta F \simeq 0.06$ Hartree a_o^{-1}, $P \gtrsim 99\%$ for collisions energies $E \lesssim 1$ KeV. Consequently

(•) Footnote : Bagus P.S., Liu B., Mc Lean A.D. and Yoshimine M. of the Th. Chem. Group at IBM research in San Jose, California. Preliminary descriptions of the Alchemy program are given by Mc Lean in " Proc. of the Conf. on Potential Energy Surfaces in Chemistry" (California Univ., Santa Cruz 1970) and by Bagus in " Selected Topics in Mol. Phys.", Berlin 1972. See also IBM Research Publication 14748 (1971).

the above crossing does not participate to the charge exchange processes in this energy range. In contrast transitions will take place at larger R where the exponentially decreasing charge exchange interaction (see fig. 1) becomes equal to half the energy splitting between the two potential energy curves (Stueckelberg 1932). One finds $R_c = 6.7\ a_o$ for the location of Demkov-type transition (Demkov 1964).

A question arises as to how this description of the near-resonant charge transfer process in H^+ - Xe collisions can be reconciled with the results of a previous description based on the molecular calculations of Kubach and Sidis (1973). It was shown in that work that charge transfer transitions were to take place around the crossing between the two $X\ ^1\Sigma^+$ and $K\ ^1\Sigma^+$ LCAO SCF potential energy curves. These two curves were found to cross at $R = 6.7\ a_o$ (•) (see fig. 1). This value agrees remarkably well with the critical region obtained above. As in both the present PVB approach and the previous LCAO SCF description the system actually evolves on the adiabatic potential energy curves for $R < R_c$ (Demkov 1964, Kubach and Sidis 1976, Benoit et al 1976) the two approaches are expected to yield similar interference patterns in the calculated differential cross sections.

Although the main coupling for charge exchange processes is confined to the two lowest $^1\Sigma^+$ PVB states (Kubach and Sidis 1976), the large spin orbit splitting of Xe^+ (^2P) requires that a three-state calculation be performed. As shown by Mies (1973) and Kubach and Sidis (1976) particular combinations of the $\tilde{I}\ ^1\Sigma^+$ and the $^3\Pi$ PVB states can provide convenient diabatic states for treating the spin-orbit effect. The lowest three $\Omega = 0^+$ diabatic potential energy curves are shown in fig. 2 . For the same reasons as discussed above the two crossings at $R = 4.a_o$ and $R = 4.5\ a_o$ are strongly avoided and the actual Demkov transitions between the $\Omega = 0^+$ states occur around $R = 9\ a_o$ (for $Xe + H^+ \longrightarrow Xe^+\ ^2P_{1/2} + H$) and $6.5.\ a_o$ (for $Xe + H^+ \longrightarrow Xe^+\ ^2P_{3/2} + H$) (see fig. 2). These values are consistent with the previous estimates ($10.\ a_o$ and $6.25\ a_o$) of the crossing radii (Kubach et al 1975).

Footnote :

(•) This value is obtained after adjustement of the calculated asymptotic energy separation between the $K\ ^1\Sigma^+$ and $X\ ^1\Sigma^+$ states to the experimental energy difference (Moore 1955). The upward shift of the $K\ ^1\Sigma^+$ curve (0.026 Hartree, Kubach et al 1975) moves the crossing location from the calculated value $R_c = 6.2\ a_o$ to $6.7\ a_o$. Such an adjustment is needless in the PVB calculation since this energy difference was in error by only 0.0038 Hartree.

The scattering quantal close-coupled equations were solved with the Gordon program (1969, 1971) as modified by Stern et al (1976). To avoid the defects of the PVB approach at small R (see fig. 1), a basis change from the LCAO - SCF - CI basis at small R to the PVB basis at large R is performed during the integration of the coupled equations (Kubach and Sidis 1976, Benoit et al 1976). The convoluted(•) differential cross sections for elastic and charge transfer processes at E = 200 eV are shown along with the experimental data of Kubach et al (1976) in fig. 3. Good agreement is obtained for the $^2P_{3/2}$ cross section in the range $\tau = E.\theta \lesssim 600$ eV. deg whereas the $^2P_{1/2}$ cross section is poorly reproduced at small reduced angles ($\tau \lesssim 150$ eV deg.).

These new calculations confirm the previous results (see fig. 7c of Kubach et al 1976) obtained with a less appropriate approach. In particular the oscillations in the cross sections can be analyzed in the same way since : i) the transition regions have the same locations and ii) the phases developed at small R are identical. In addition it has been shown that charge transfer in H^+ - Xe collisions is understandable as occuring under Demkov-type transitions as it is the general rule for the lighter H^+ + rare gas systems (Benoit et al 1976).

It can finally be noticed as a general conclusion that the PVB method could even be extented to systems involving nuclei of similar masses (for example H^+ - He). Although in such cases the d/dR coupling (e. g. $\langle \widetilde{1s}_H | d/dR | 1s_{He} \rangle$) is no more negligible it could be calculated very easily since the difficulty of numerically differentiating the MO expansion coefficients over atomic orbitals is avoided here by the use of a constant orbital (e. g. $1s_{He}$). Diabatic states can then be found by a minimization of the above coupling.

(•) Footnote : The convolution over angle is carried out by assuming a gaussian apparatus function having 0.2 deg full width at half-maximum

REFERENCES

- Benoit C., Kubach C., Sidis V., Pommier J., and Barat M., 1976 submitted to J. Phys. B. Atom. molec. Phys.

- Demkov Yu N. 1964, Sov. Phys. J.E.T.P. 18 138-42.

- Gordon R.G. 1969. J. Chem. Phys. 51 14-25.
  1971. Meth. Comput. Phys. 10 81-109.

- Kubach C. and Sidis V 1973 J. Phys. B : Atom. Molec. Phys. 8 L 289-93.

- Kubach C., Sidis V. and Durup J. 1975 J. Phys. B : Atom. Molec. Phys., 8, 1129 - 38.

- Kubach C. and Sidis V. 1976 Phys. Rev. A. (in press).

- Kubach C., Benoit C., Sidis V., Pommier J. and Barat M. 1976 J. Phys. B : Atom. Molec. Phys. (in press).

- Landau L. 1932 Phys. Z Sowjun 2 46-51.

- Mies F.M. 1973 Phys. Rev A 7 942-57.

- Moore C.E. Atomic Energy levels, N.B.S. Circular No 467 vol. 3 (Washington, D.C. : U S Govt Printing office).

- Smith F.T. 1969 Phys. Rev. A 119 111-23.

- Stern B., Gauyacq J.P. and Sidis V. 1976 to be published.

- Stueckelberg E.C.G. 1932. Helv. Phys. Acta. 5 369-422.

- Zener C. 1932. Proc. R. Soc. A 137 696-702.

FIGURE CAPTIONS

Fig. 1 a $^1\Sigma^+$ potential energy curves of the H^+ - Xe system.
-·-·-Present diabatic PVB calculation.
·····LCAO SCF results (Kubach and Sidis 1973).
——— SCF CI results, (•) PVB CI results,
the arrow shows the location of the transtion region.

b Calculated coupling $\langle \tilde{X}\,^1\Sigma^+ | H_{el} | \tilde{I}\,^1\Sigma^+ \rangle$

$\Delta E/2$ definies the critical internuclear distance R_c.

Fig. 2 Three lowest $\Omega = 0^+$ diabatic potential energy curves of the H^+ - Xe system. The arrows show the location of the transition regions

Fig. 3 Convoluted reduced differential cross sections calculated a E = 200 eV. (——) elastic, (▬▬) $^2P_{1/2}$ charge exchange (-----) $^2P_{3/2}$ charge exchange. Dots and triangles refer respectively to the $^2P_{1/2}$ and $^2P_{3/2}$ cross section data of Kubach et al 1976.

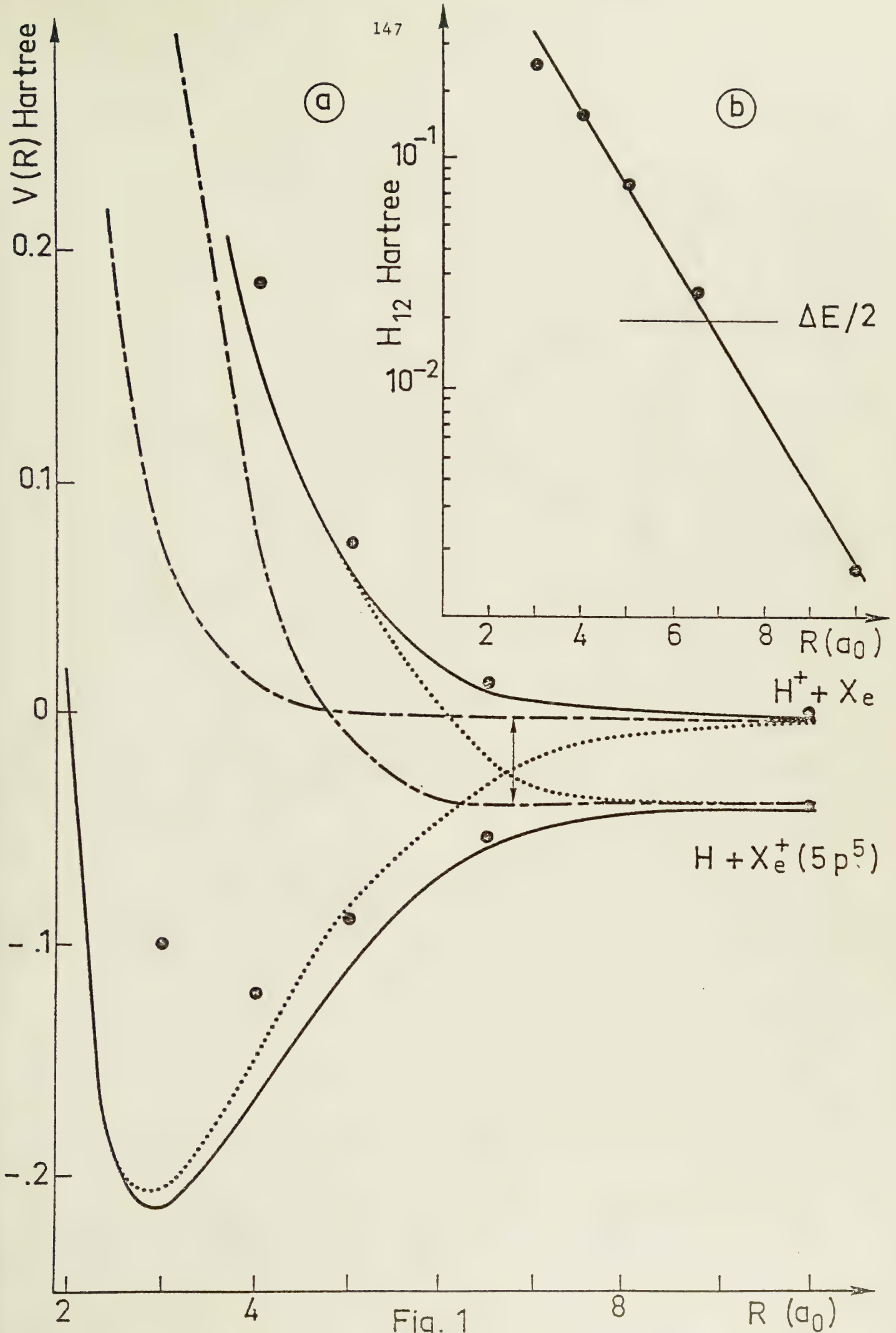

V(R) Hartree
0.2
0.1
0
-.1
-.2
2
4
8
R (a0)
a
b
H12 Hartree
10-1
10-2
ΔE/2
2
4
6
8
R(a0)
H+ + Xe
H + Xe+(5p5)

Fig. 1

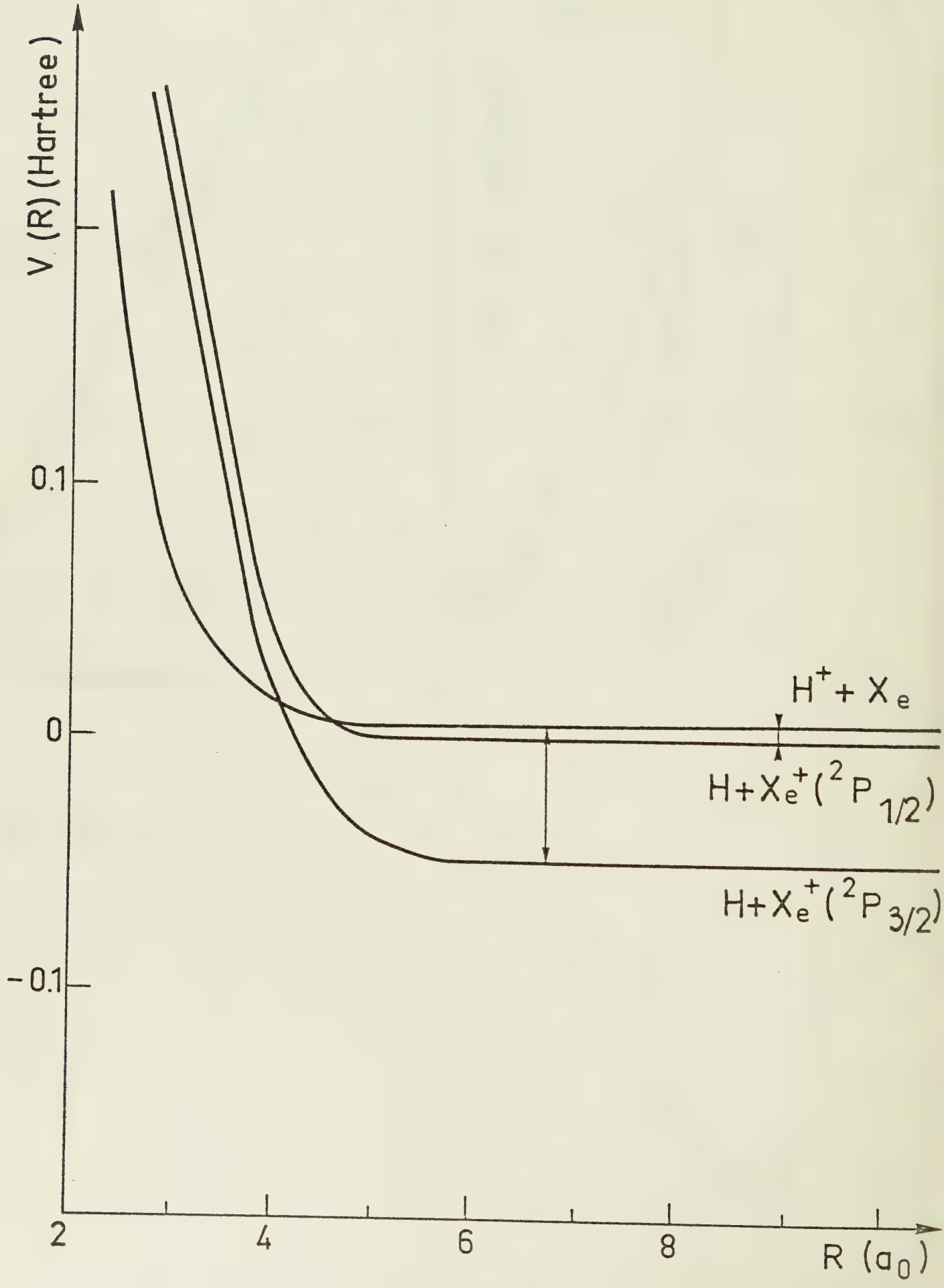


Fig. 2

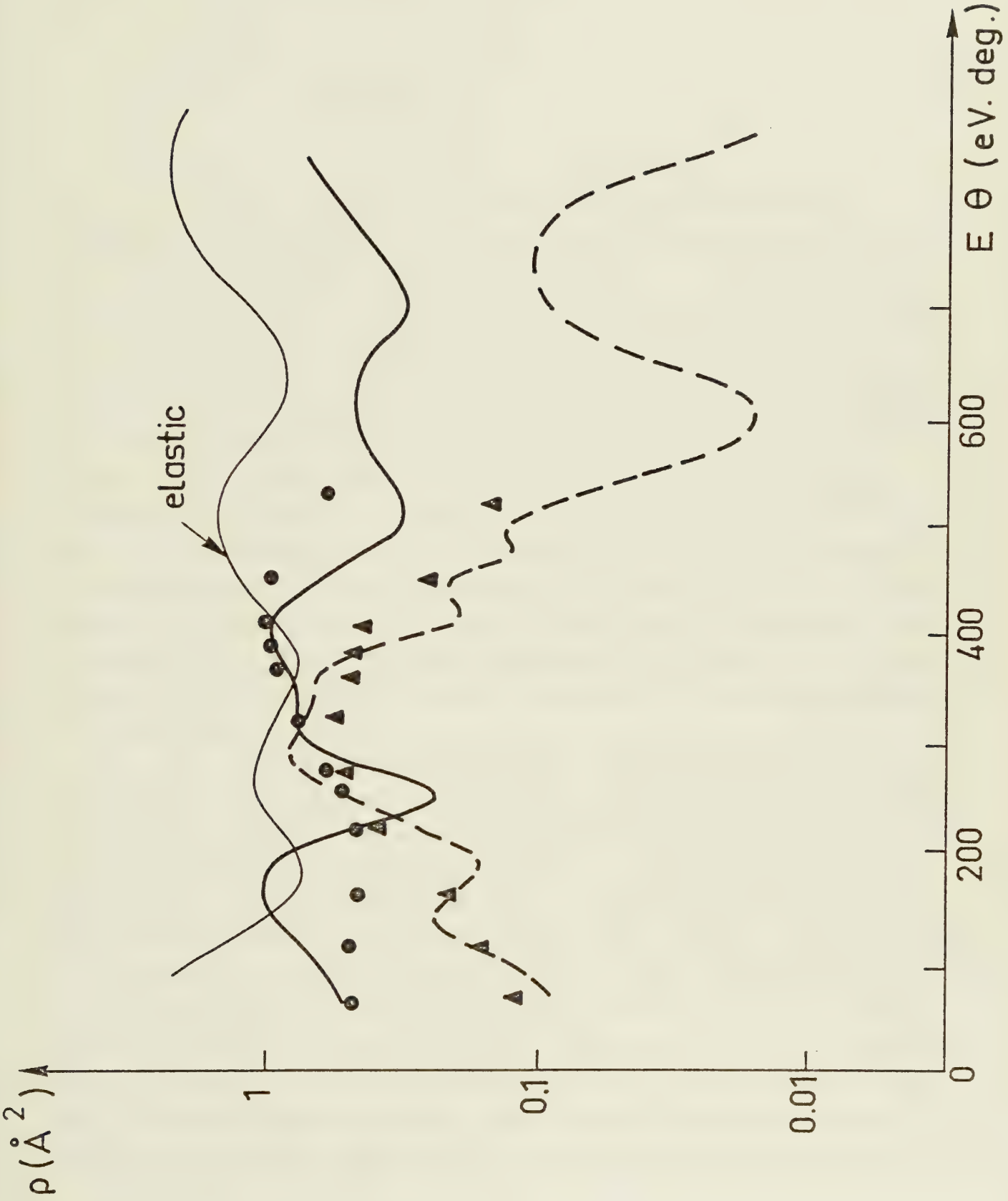


Fig. 3

Chapitre X

CONCLUSION

Le travail présenté ici constitue une contribution à la compréhension des processus collisionnels et à la façon d'appréhender les collisions atomiques à des énergies modérées.

A travers une étude limitée aux processus élastique et d'échange de charge quasi-résonnant dans les collisions de protons (H^+) sur des atomes de gaz rare (GR), nous avons rencontré quelques uns des mécanismes importants de la physique des collisions. C'est ainsi que les processus d'excitation par croisement de courbes d'énergie potentielle et/ou par transitions semi-localisées ont été étudiés respectivement dans le système H^+ - Xe et dans l'ensemble des systèmes de la série H^+ - GR. Le couplage rotationnel qui, dans les collisions H^+ - GR, ne participe qu'à des processus secondaires, a été abordé dans une étude complémentaire du système H^+ - H. En nous appuyant sur des modèles existants (modèle Landau - Zener - Stueckelberg, modèle de Demkov), nous avons pu cerner les mécanismes de la collision. Les calculs entrepris par la suite nous ont permis de discuter la valeur de ces modèles pour des exemples concrets.

Nous avons bénéficié, d'une part, de résultats expérimentaux très fins qui constituent le meilleur test pour les calculs entrepris et, d'autre part, des progrès réalisés dans la technique des méthodes de résolution des équations quantiques couplées. Actuellement, la résolution des équations décrivant la collision ne constitue plus un problème majeur, si l'on excepte certaines difficultés relatives à la façon de tenir compte de l'effet d'entraînement des électrons par les noyaux. Le choix des méthodes, quantiques ou semi-classiques, de traitement de la diffusion n'est plus qu'une question d'école et de compétitivité des programmes disponibles. Le problème le plus délicat, et peut-être le plus intéressant à résoudre, demeure celui de l'obtention d'une base adéquate d'états électroniques permettant de résoudre les équations couplées et de comprendre les mécanismes collisionnels.

Si les états construits à l'aide d'orbitales moléculaires sont bien adaptés à la description du puits de potentiel et, d'une façon générale, au traitement des distances internucléaires petites et moyennes, ils ne constituent pas la meilleure approche pour traiter les processus d'échange de charge quasi-résonnant dans les systèmes du type H^+ - GR. En effet, une telle approche requiert l'inclusion d'un état diexcité "relais" et l'onéreux calcul du couplage radial entre les orbitales moléculaires. Par contre, nous avons montré que les états PVB, qui préservent les caractéristiques atomiques, sont bien adaptés à la description du domaine des grandes distances internucléaires où ont lieu les transitions responsables de l'échange de charge quasi-résonnant. Les états PVB, qui concilient les idées originales de O'Malley et de Smith, constituent une contribution à la recherche d'états diabatiques. Un autre intérêt des états PVB réside dans le fait que ce sont eux qui sont invoqués dans la théorie de l'échange de charge quasi-résonnant de Demkov. Nous avons pu ainsi vérifier par le calcul ab-initio les hypothèses du modèle échafaudé par cet auteur où les transitions responsables de l'échange de charge s'effectuent entre deux états de même symétrie ayant des courbes de potentiel parallèles et une intéraction exponentiellement décroissante avec la distance internucléaire.

Nous avons montré, en accord avec les idées de Demkov, qu'il y avait complémentarité entre deux notions opposées : l'aspect moléculaire à petite distance internucléaire et l'aspect atomique à grand R. Pour tenir compte de cette dualité, on est amené à effectuer un changement de base afin d'avoir une description appropriée dans chacun de ces domaines. En fait, la notion de changement de base est tout-à-fait générale aux problèmes de collision. Ainsi que l'avait noté Hund, il parait en effet assez présomptueux d'espérer construire une base finie d'états électroniques apte à décrire tout le domaine des distances internucléaires, quel que soit le processus considéré et les mécanismes d'excitation mis en jeu.

Les processus d'échange de charge quasi-résonnant présentent l'avantage de mettre en jeu des transitions semi-localisées. Ceci permet une compréhension semi-classique assez immédiate de l'évolution du système collisionnel et conduit donc à une analyse simple des oscillations dans les sections efficaces calculées et expérimentales, en termes d'oscillations de type arc-en-ciel et de type Demkov-Stueckelberg.

Les résultats présentés ici mettent en évidence l'unicité du type de mécanismes d'échange de charge dans les collisions H^+ - GR. Les transitions responsables de ce processus sont de type Demkov pour toute la série H^+ - GR, y compris le xénon. Ceci a été vérifié par le calcul ab-initio sur les systèmes H^+ - Xe et H^+ - Kr. De plus, nous avons montré comment la compréhension des processus d'échange de charge dans ces deux systèmes permettait, en s'appuyant sur des modèles existantsdans la littérature, une extrapolation aux systèmes plus légers. Il apparaît aussi que, dans la série H^+ - GR, le xénon ne constitue une exception que pour le processus élastique à faible énergie. En effet, l'existence de croisements très fortement évités particuliers à ce système, fait que, même à quelques eV, on ne peut pas décrire la diffusion élastique à l'aide d'un potentiel unique. La mesure des sections efficaces différentielles élastiques ne permet donc pas une détermination du puits de potentiel de $(H\text{-}Xe)^+$, alors que cette estimation est possible pour tous les autres systèmes de la série $(H\text{-}GR)^+$.

L'accord entre les sections efficaces calculées et expérimentales pourrait, bien sûr, être amélioré au prix d'un plus gros effort. Il faudrait, en effet, tenir compte des couplages rotationnels secondaires entre états ayant la même limite de dissociation. La prise en considération de ces processus secondaires permettrait de traiter complètement les problèmes de polarisation mais nécessiterait, par contre, un important accroissement de la taille des calculs.

Nous espérons avoir montré que les états PVB permettent une description attrayante et très efficace des processus d'échange de charge dans les collisions H^+ - GR. Il nous paraît souhaitable qu'un tel traitement soit généralisé à d'autres systèmes afin d'obtenir des informations complémentaires sur les problèmes de corrélation des états diabatiques. Ainsi, la méthode PVB appliquée au système He^+ - Ar, ou à d'autres systèmes très dissymétriques, qui ont nécessité la modification des règles de corrélation des orbitales diabatiques, devrait fournir des éléments de réponses quantitatives à ces problèmes.

REFERENCES

1. J.B. Stedefort et J.B. Hasted, 1955, Proc. Roy. Soc. A 227, 466.
2. P.M. Stier et C.F. Barnett, 1956, Phys. Rev. 103, 8986.
3. G.J. Williams et D.N. Dunbar, 1966, Phys. Rev. 149, 62.
4. F.J. De Heer, J. Schutten et H. Moustafa, 1966, Physica 32, 1766.
5. D.W. Koopman, 1967, Phys. Rev. 154, 79.
6. D.C. Lorents et W. Aberth, 1965, Phys. Rev. A 139, 1017.
7. H.H. Fleischmann et R.A. Young, 1967, Phys. Rev. Letters 19, 941.
8. R.L. Champion, L.D. Doverspike ,W.G. Rich et S.M. Bobbio, 1970, Phys. Rev. A 2, 2327.
9. H.P. Weise, H.P. Mittmann, A.Ding et A. Henglein, 1971, Z. Naturf. 26a, 1112.
10. W.G. Rich, S.M. Bobbio, R.L. Champion et L.D. Doverspike,1971, Phys. Rev. A 4, 2253.
11. M. Abignoli, M. Barat, J. Baudon, J. Fayeton et J.C. Houver, 1972, J. Phys. B 5 , 1533.
12. M. Barat et W. Lichten, 1972, Phys. Rev. A 6, 219.
13. J.C. Brenot, J. Pommier, D. Dhuicq et M. Barat, 1975, J. Phys. B. 3,448.
14. C. Benoit, J.C. Brenot, J. Pommier, M. Barat et E. Pollack, 1974, J. Phys. B. 7, L 424.
15. H. Faxen et J. Holzmark, 1927, Physik 45, 307.
16. R.C. Langer, 1937, Phys. Rev. 5, 669.
17. H.H. Michels, 1966, J. Chem. Phys. 44, 3834.
18. L. Wolniewicz, 1965, J. Chem. Phys. 43, 1087.
19. S. Peyrimhoff, 1965, J. Chem. Phys. 43, 998.
20. V. Sidis, 1972, J. Phys. B. 5, 1517.

21. S.M. Bobbio, W.G. Rich, L.D. Doverspike et R.L. Champion, 1971, Phys. Rev. A 4, 957.

22. E.C.G. Stueckelberg, 1932, Helv. Phys. Acta 5, 369.

23. N. Rosen et C. Zener, 1932, Phys. Rev. 40, 502.

24. E.F. Gurnee et J.L. Magee, 1957, J. Chem. Phys. 26, 1237.

25. D. Rapp et N.E. Francis, 1962, J. Chem. Phys. 37, 2631.

26. Yu. N. Demkov, 1964, Sov. Phys. JETP 18, 138.

27. D. Rapp et J.B. Ortenburger, 1960, J. Chem. Phys. 33, 1230.

28. T.A. Green et R.E. Johnson, 1966, Phys. Rev. 152, 9.

29. H.P. Weise, 1971, thèse (Berlin).

30. R.E. Johnson, C.E. Carlson et J.W. Boring, 1972, Chem. Phys. Letters 16, 1129.

31. R. Shakeshaft et J. Macek, 1972, Phys. Rev. A 6, 1876.

32. R.E. Olson, 1972, Phys. Rev.A 6, 1822.

33. R.E. Olson, F.T. Smith et E. Bauer, 1971, Appl. Opt. 10, 1848.

34. N.F. Mott, 1931, Proc. Phil. Soc. 27, 553.

35. W. Lichten, 1963, Phys. Rev. 131, 229.

36. F.T. Smith, 1969, Phys. Rev. A 179, 111.

37. D.R. Bates, 1958, Proc. Roy. Soc. (Londres) A 247, 294.

38. D.R. Bates et R. Mc Carroll, 1958, Proc. Roy. Soc. (Londres) A 245, 175.

39. Gaussorgues, C. Le Sech, F. Masnou-Seeuws, R Mc. Carroll et A. Riera, 1975, J. Phys. B 8, 239.

40. S.K. Knudson et N.R. Thorson, 1970, Can. J. Phys. 48, 313.

41. N. Lane et S. Geltman, 1967, Phys. Rev. 160, 53.

42. R.G. Gordon , 1969, J. Chem. Phys. 51, 14.
1971, Meth. Comput. Phys. 10, 81.

43. N.R. Thorson, 1961, J. Chem. Phys. 34, 1744.

44. J. Durup, 1976, non publié.

45. B. Andersen et S.E. Nielsen ,1971, Molec. Phys. 21, 523.

46. V. Sidis, 1975, Thèse de doctorat d'état (Paris).

47. V. Sidis, 1975, The Physics of Electronic and Atomic Collisions, invited lectures and progress reports p. 295 (S. Risley et R. Geballe) Seattle.

48. J. Von. Neumann et E.P. Wigner, 1929, Physik Z. 30, 467.

49. J.N. Bradsley, 1971, Phys. Rev. A 3, 1317.

50. R.P. Feynman, 1939, Phys. Rev. 56, 340.

51. T.F. O'Malley, 1964, J. Chem. Phys. 51, 322.

52. U. Fano et W. Lichten, 1965, Phys. Rev. Letters. 14, 627.

53. M. Barat, 1973, The Physics of Electronic and Atomic Collisions, invited lectures and progress reports p. 44 (Cobic et Kurepa) Belgrade.

54. N. Aubert et C. Le Sech, 1976, Phys. Rev. A 13, 632.

55. J S. Briggs, 1975, The Physics of Electronic and Atomic collisions Invited lectures and Progress Report p. 394. (S. Risley and R. Geballe) Seattle.

56. K. Taulbjerg et J.S. Briggs 1975, J. Phys. B. 8, 1895.

57. J.P. Gauyacq travail en cours.

58. J. Fayeton, N. Andersen et M. Barat, 1976, J. Phys. B 9, L 149.

59. V. Sidis, N. Stolterfoht et M. Barat, travail en cours.

60. F. M. Mies, 1973, Phys. Rev. A 7, 942.

61. C.C.J. Roothaan 1951, Rev. Mod. Phys. 23, 69.

62. V. Sidis et H. Lefebvre-Brion, 1971, J. Phys. B. 4, 1040.

63. J.C. Slater, Quantum theory of Molecules and Solids (vol. 1) Mc Graw Hill Book Company, Inc.

64. I. Ja Berson, 1968 Latv PSR Zin Akad. Vestis. Fiz. Techn. 4, 47.

65. W. Thorson, J.B. Delos et S.A. Bernstein, 1971, Phys. Rev. A 4, 1052.

66. B.B. O'Shea. Algorithms for the solution of systems of coupled second order ordinary differential equations. Univ. of Nebraska.

67. A.C. Allison, 1970, J. Comp. Phys. 6, 375.

68. I.H. Sloan 1964, Proc. Roy. Soc. (Londres) A 281, 151.

69. I.H. Sloan 1968, J. Comp Phys. 3, 40.

70. S.A. Evans, T.S. Cohen et N.F. Lane, 1971, Phys. Rev. A 4, 2235

71. N.F. Mott et H.S.W. Massey 1965, the theory of atomic collisions (third edition) Oxford Clarendon Press.

72. C. Kubach, 1974, Thèse de troisième cycle (Paris).

73. B. Stern, J.P. Gauyacq et V. Sidis (1976), en cours de publication.

74. J. Durup, 1974, non publié.

75. D.R. Bates et D.A. Williams, 1964, Proc. Phys. Soc., 83, 425.

76. R. Mc Carroll (97) The Physics of Electronic and Atomic collisions Invited Lectures and Progress Reports, p. 71 (Cobic et Kurepa) Belgrade.

77. W. Lichten, 1967, Phys. Rev. A 164, 131.

78. T.S. Briggs et J. Macek 1973, J. Phys. B 6, 982.

79. J.S. Briggs and K. Taulbjerg 1975, J. Phys. B 8, 1909.

80. K. Taulbjerg J.S. Briggs et J. Vaaben, 1976, J. Phys. B 9, 1351.

81. L. Landau et E. Lifchitz, 1969, Mécanique (3ème édition). Edition MIR, (Moscou)

82. J.S. Briggs and J.H. Macek, 1972, J. Phys. B 5, 579.

83. C. Gaussorgues, C. Le Sech, F. Masnou-Seeuws, R. Mc Carroll et A. Riera, 1975, J. phys. B 8, 253.

84. C. Gaussorgues, 1973, J. Phys. B 6, 675.

85. R.E. Olson et F.T. Smith, 1971, Phys. Rev. A 3, 1607.

86. J.B. Delos et W. Thorson, 1972, Phys. Rev. A 6, 709.

87. J.B. Delos, W. Thorson et S. Knudson, 1972, Phys. Rev. A 6, 720.

88. J.B. Delos et W. Thorson, 1972, Phys. Rev. A 6, 728.

89. E.E. Nikitin, 1968, Chemische Elementarprozesse, ed. by Hartmann, (Berlin : Springer-Verlag) p. 43.

90. L. Landau 1936, Phys. Z. Sowjun, 2, 46.

91. C. Zener, 1932, Proc. Roy. Soc. A 137, 696.

92. R. Daudel, R. Lefebvre et C. Moser, quantum chemistry (Interscience, New York 1959) p. 475.

93. E. Ishiguro et M. Kobori 1967, J. Phys. Soc. Japan, 22, 263.

94. C. Moore, 1958, Atomic Energy Levels. National Bureau of Standards,

95. F. Masnou Seeuws, 1973, Thèse de doctorat d'état (Paris).

96. J.P. Gauyacq, travail en cours.

97. P. Fournier, C. Benoît, J. Durup et R. March, 1974, C. R. Acad. Sciences B -1039.

98. B.M. Smirnov, 1968, Atomic collision and Elementary Process in Plasma (Atomizdat, Moscou).

99. L. Pauling et E.B. Wilson, 1935, Introduction to quantum mechanics (Mc Graw-Hill Book- Company. Inc. New York) p. 138.

UNIVERSITE DE PARIS-SUD

CENTRE D'ORSAY

1725

PERMIS D'IMPRIMER

Doctorat d'ETAT

Thèse de SCIENCES PHYSIQUES (Chimie)

Nom KUBACH

Prénoms Christian Jean

Date et lieu de naissance 14 Mai 1947 à SAINT GERMAIN EN LAYE (Yvelines)

SUJET :

Thèse : Etude théorique des processus élastique et d'échange de charge dans les collisions de protons sur des atomes de gaz rares.

UNIVERSITÉ PARIS-SUD ★ ORSAY

Vu et approuvé :

Orsay, le 20 OCTOBRE 1976

Les Membres du Jury.

Service de Reprographie
C . N . R . S .
Gif